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1 **Investigation of subglacial weathering under the Greenland Ice Sheet using**

2 **silicon isotopes.**

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39 **Abstract**

40 **Subglacial chemical weathering plays a key role in global silicate weathering budgets,**

41 **contributing to the cycling of silicon (Si) in terrestrial and marine systems and the potential**

42 **drawdown of carbon dioxide from the atmosphere. Here, we use data from two Greenland Ice**

43 **Sheet (GrIS) catchments to demonstrate how Si isotopes from dissolved and amorphous**

44 **particulate fractions (δ^{30}DSi and δ^{30}ASi respectively) can be used together with major ion data**

45 **to assess the degree of secondary silicate weathering product formation and redissolution in**

46 **subglacial environments. We compare a time-series of summer melt seasons from the two study**

47 **sites, which differ in catchment size (~600 km^2 for Leverett Glacier (LG) and ~36 km^2 for**

48 **Kiattuut Sermiat (KS)). Subglacial waters from LG have elevated Na$^+$ and K$^+$ ions in relation to**

49 **Ca^{2+} and Mg^{2+} ions, indicating a predominance of silicate weathering, whilst meltwaters from**

50 **KS are characterised by carbonate weathering (hydrolysis and carbonation) throughout the**

51 **melt season. Both catchments have mean δ^{30}DSi values substantially lower than average riverine**

52 **values (KS 0.41‰, LG -0.25‰, versus a global riverine mean of 1.25‰) and display a seasonal**

53 **decline, which is more pronounced at LG. The δ^{30}ASi values (discharge weighted mean values**

54 **KS -0.44‰, LG -0.22‰) are lighter than the bedrock (mean values KS -0.18±0.12‰, LG**

55 **0.00±0.07‰) in both catchments, indicating a secondary weathering product origin or leaching**

56 **of lighter isotopes during initial weathering of crushed rock. When used in combination, the**

57 **major ion and silicon isotope data reveal that the extent of silicate weathering and secondary**

58 **phase redissolution are more pronounced at LG compared to KS. Contrasting weathering**

59 **regimes and subglacial hydrology between catchments need to be considered when estimating**

60 **the δ^{30}Si composition of silica exported into polar oceans from the GrIS, with larger catchments**

61 **likely to produce fluxes of lighter δ^{30}Si. As larger catchments dominate freshwater export to the**

62 **ocean, GrIS meltwater is likely to be very light in isotopic composition, and the flux is likely to**

63 **increase with ice melt as the climate warms.**

64

65 ## 1. Introduction

66 The weathering of silicate minerals plays an important role in biogeochemical cycles, producing

67 dissolved silicate (DSi) and dissolvable amorphous silica (ASi) into terrestrial and marine systems,

68 whilst consuming carbon dioxide (CO_2) (Walker et al., 1981; Berner, 2003). DSi is generated through

69 physical weathering and the subsequent chemical dissolution of silicate minerals, and then mobilised

70 via fluvial hydrological systems. Primary weathering processes also lead to secondary mineral

71 formation. Secondary weathering products, such as clays and ASi have varying solubility and may

72 contribute DSi to the fluvial system through redissolution processes (Frings et al., 2016). The resultant

73 DSi is converted to biogenic silica (BSi) by siliceous organisms, including diatoms, which are

74 responsible for 35-70% of oceanic productivity (Nelson et al., 1995). Weathering processes,

75 precipitation, and biogenic uptake result in fractionation of silicon isotopes, meaning isotopic analysis

76 can provide insight into the weathering regimes and biological utilisation of Si within aquatic systems

77 (De la Rocha et al., 1997; De La Rocha et al., 2000; Fontorbe et al., 2013; Frings et al., 2016).

78 Glaciation promotes physical and chemical weathering, with dynamic hydrological and microbial

79 systems upon, within and beneath ice (Wadham et al., 2010; Tranter and Wadham, 2014). It is likely

80 that weathering beneath large ice sheets is silicate mineral dominated (Stevenson et al., 2017), due to

81 the enhanced residence times of subglacially stored waters, which result in exhaustion of carbonate

82 minerals or saturation of meltwaters with respect to calcite (Wadham et al., 2010; Hindshaw et al.,

83 2014; Michaud et al., 2016). This is evidenced by the ionic composition of meltwaters (high relative

84 proportions of Na^+ and K^+) from the bed of the Greenland Ice Sheet (GrIS) (Graly et al., 2014) and the

85 Antarctic Ice Sheet (AIS) (Michaud et al., 2016) compared to Alpine valley glaciers. Recently, there

86 has been increased focus on the chemical composition of GrIS meltwaters in an attempt to improve

87 the understanding of weathering processes in large ice sheet catchments and associated nutrient

88 release (Graly et al., 2014; Hindshaw et al., 2014; Yde et al., 2014; Graly et al., 2017; Kohler et al.,

89 2017). High fluxes of Si resulting from weathering processes have been reported from ice sheets. For

90 example, Hawkings et al. (2017) estimated silica fluxes from GrIS to be approximately 50% of input

91 from Arctic rivers (0.20 Tmol year[1]). However, the mechanisms and control on silicate dissolution

92 processes in ice sheet catchments are currently poorly understood, which is compounded by the

93 difficulty of acquiring data over an entire melt season and across differing hydrological regimes in

94 challenging environments. An improved understanding of the complex nature and extent of subglacial

95 silicate weathering is necessary to fully understand and quantify silicon cycling on a global scale

96 (Graly et al., 2014; Hindshaw et al., 2014; Yde et al., 2014).

97 Silicon isotopes (denoted by $\delta^{30}Si$) are increasingly used as a tool for studying continental weathering

98 (Ding et al., 2004; Georg et al., 2007; Opfergelt et al., 2013; Chemtob et al., 2015), especially in

99 riverine systems (Ding et al., 2004; Cardinal et al., 2010; Ding et al., 2011; Fontorbe et al., 2013;

100 Frings et al., 2016). Silicon has three stable isotopes; ^{28}Si, ^{29}Si and ^{30}Si with relative abundances of

101 92.2%, 4.7% and 3.1% respectively (Ding et al., 2005). The isotopic composition is reported relative

102 to international reference standard NBS-28, as a deviation from the ratio of $^{28}Si/^{30}Si$ of the sample

103 from the reference standard (Equation 1, Frings et al. 2016). The isotopic composition of the lower

104 crust (-0.29±0.04‰), middle crust (-0.23±0.04‰) and bulk earth values (-0.29±0.08‰) are well

105 characterised (Savage et al., 2010; Savage et al., 2013). Relatively large fractionation occurs during

106 weathering processes as newly formed secondary weathering products are enriched with lighter

107 isotopes (Andre et al., 2006; Frings et al., 2016). The range of DSi isotopic compositions in rivers

108 draining from non-glaciated catchments is currently 0.4-3.4‰ (De La Rocha et al., 2000; Ding et al.,

109 2004; Cardinal et al., 2010; Ding et al., 2011), with a global mean of 1.25±0.68‰ (Frings et al., 2016).

110 Riverine DSi is therefore generally enriched in the ^{30}Si isotope compared with bulk silicate earth and

111 suspended particulate matter, which is isotopically lighter on average (-0.18‰, Frings et al., 2016;

112 Ding et al. 2004). Precipitated silica from the formation of secondary weathering or biological uptake

113 is enriched in ^{28}Si, due to preferential uptake of the lighter isotope, resulting in an enrichment of ^{30}Si

114 in the dissolved phase (De la Rocha et al., 1997; De La Rocha et al., 2000; Ziegler et al., 2002; Ding

115 et al., 2004). However, whilst these generalisations about the fractionation of low temperature

116 processes can be made, more definite fractionation factors for many environmental processes are still

117 very uncertain (Frings et al., 2016).

118 Studies of Icelandic rivers have shown that catchments with greater glacial coverage have a lighter

119 dissolved $\delta^{30}Si$ composition ($\delta^{30}DSi$) compared to non-glacial rivers (Georg et al., 2007). Opfergelt et

120 al. (2013) reported glacial rivers to have a mean composition of 0.17 ± 0.18‰ compared to 0.97 ±

121 0.31‰ for non-glacial rivers. The dissolved phase exported from a large ice sheet catchment of GrIS

122 has also been shown to have an isotopic composition lighter than the bulk bedrock (-0.25 ± 0.12‰

123 compared to 0.00 ± 0.07‰, Hawkings et al., 2018). These studies indicate that subglacial processes

124 could be influencing the isotopic composition of meltwaters. Si isotope systematics could potentially

125 be used to provide insight into silicate dissolution and redissolution of secondary weathering products

126 within the subglacial environment. However, we currently lack high resolution time series data to

127 show whether these patterns are consistent across glacial catchments and to explain the mechanism

128 driving the export of low δ^{30}Si. We need to gain a better understanding of subglacial biogeochemical

129 processes, and their impact on the δ^{30}Si compositions of exported dissolved and particulate phases.

130 This will allow us to quantify the impact of Si exported from GrIS on the wider silica cycle and make

131 predictions about how export from large ice sheets may change over longer timescales.

132 Here we combine new δ^{30}Si measurements of DSi and ASi phases with hydrogeochemical data from

133 GrIS glacial catchments of contrasting scale over the summer melt season, in order to improve the

134 current understanding of subglacial weathering processes.

2. Methodology

2.1 Sampling locations

137 We present hydrological and geochemical data from two polythermal- based, land terminating outlet

138 glaciers from the GrIS, both of which have subglacial drainage systems that develop seasonally

139 (Bartholomew et al., 2011). Data were collected from the proglacial river exiting Kiattuut Sermiat

140 (KS; 61.2°N, 45.3°W; Fig. 1) from April to August 2013 and Leverett Glacier, (LG; 67.06°N,

141 50.17°W; Fig. 1) from May to July 2015 to capture the composition of meltwaters exiting the glaciers

142 during the summer ablation season. KS is a small coastal glacier, covering an area of 36km^2 and

143 currently terminating in a proglacial lake of approximately 0.5km^2 (Hawkings et al., 2016; Dubnick et

144 al., 2017). Calculations using discharge records find the turnover time of the proglacial lake to be

145 relatively short once the glacial melt season begins (less than 24 hours from Day 157, Supplementary

146 Fig. 1), indicating that the lake will likely not have a significant effect on the meltwater chemistry

147 downstream. In comparison, LG is a much larger glacier, with a hydrologically active catchment of

148 around 600km^2 (Cowton et al., 2012), which feeds into Watson River and then into the Davis Strait

149 via the Søndre Strømfjord (Hawkings et al., 2016). The composition of bedrock beneath LG is

150 dominated by Precambrian Shield crystalline gneiss and granite, which is representative of the

151 majority of GrIS (Escher, 1976) and much of the bedrock that was covered by the Eurasian and North

152 American Ice Sheets (Bouysse, 2014). The bedrock at KS is relatively similar to LG, but there are

153 some potential differences. KS overlays the Gardar Province, containing basalts, trachytes and

154 phonolites. This region may also include syenites from the intrusive rocks of the Julianhåb batholith

155   (Henriksen, 2009). However, previous work on δ^{30}Si fractionation and elemental differentiation

156   during high temperature processes in the mantle has shown limited isotope fractionation in

157   comparison to weathering and biological processes (Savage et al., 2010).

158   We carried out hydrological monitoring of discharge, suspended sediment, pH and electrical

159   conductivity using *in-situ* hydrochemical sensors (Fig. 1), as detailed by Kohler et al. (2017) and

160   Hawkings et al. (2018). Water samples were collected at least once a day from just below the surface

161   of the proglacial river using 1L Nalgene™ bottles (HDPE). Samples were filtered immediately using

162   0.45µm cellulose nitrate membrane filters (Whatman®) mounted on a PS filtration stack (Nalgene™)

163   and kept refrigerated in the dark until laboratory analysis. Samples for ASi concentrations and

164   amorphous isotopic composition (δ^{30}ASi) were collected by filtering approximately 500ml of the

165   same water sample collected for dissolved analysis through a 0.45µm cellulose nitrate membrane

166   filters (Whatman®), retaining the sediment. Filters were kept refrigerated and in the dark until being

167   gently air dried under a laminar flow hood prior to laboratory analysis.

168

169   **2.2 Major Ion Composition**

170   Water samples were analysed for major cation (Na^+, K^+, Ca^{2+} and Mg^{2+}) and anion (NO_3^-, SO_4^{2-} and

171   Cl^-) concentrations by ion chromatography, with HCO_3^- estimated using the charge deficit (Tranter et

172   al., 2002). Measurements were carried out using a Thermo Scientific™ Dionex™ capillary ICS-5000

173   fitted with anion and cation columns (Hawkings et al., 2015; Dubnick et al., 2017).

174

175   **2.3 Silica concentrations**

176   DSi concentrations were determined spectrophotometrically using Flow Injection Analysis (FIA) on a

177   LaChat 8500 series (QuikChem Method 31-114-27-1-D), as outlined by Hawkings et al. (2017). The

178   limit of detection was 0.3µM. Precision and accuracy ($\pm0.54\%$ and $\pm1.9\%$) were determined by repeat

179   measurements of a gravimetrically weighed 8.9µM standard (n=17). ASi was determined using an

180   alkaline extraction method adapted from DeMaster (1981), as used by Hawkings et al. (2017). ASi

181   was extracted from the suspended sediments collected on 0.45µM filters in the field. Briefly, 50ml

182   0.1M Na_2CO_3 was added to ~30mg (accurately weighed) of sediment at 85°C with 1ml aliquots taken

183   at 2, 3 and 5 hours. Aliquots were neutralised immediately with 0.021M HCl and stored at 4°C until

184   FIA analysis, using the same method as DSi concentrations. ASi (wt%) was calculated following

185   DeMaster (1981). Na_2CO_3 was preferred over NaOH extractions as it is the most commonly used

186   alkaline extraction method of aquatic sediments, and is calibrated to clay minerals (Conley, 1998;

187   Sauer et al., 2006; Hawkings et al., 2017). However, a 0.2M NaOH extraction method was required to

188   extract the total reactive silica for silicon isotope analysis and both methods have been compared to

189   ensure consistency between the ASi concentrations reported and the ASi extracted for silicon isotope

190   analysis. The NaOH extraction produced similar or slightly lower concentrations compared to the

191 Na_2CO_3 method (Hawkings et al., 2018). Saturation indices for ASi were calculated for each

192 timepoint using hydrochemical data from KS and LG and Debye-Hückel ion interaction model in

193 Geochemists Workbench® Student Edition.

194

2.4 Silicon Isotope Composition

196 All silicon isotope analysis was completed in the Bristol Isotope Group laboratories (University of

197 Bristol) using a Thermo Scientific™ Neptune Plus™ High Resolution MC-ICP-MS and a standard-

198 sample-standard bracketing procedure with Mg doping (100µl 10ppm Mg) to correct for mass bias

199 (Cardinal et al., 2003; Hendry and Robinson, 2012). International reference standard NBS-28 (NIST

200 RM8546, purified quartz sand) was used as the bracketing standard and isotope compositions are

201 reported in terms of $\delta^{30}Si$ (Equation 1). Samples were doped with 50-100µL 0.1M sulphuric acid

202 (Romil-UpA) to ensure matrix match between sample and standard, to reduce the mass bias effects of

203 anion loading (Hughes et al., 2011). Instrument blanks were <1% of ^{28}Si signal and typical internal

204 reproducibility was ±0.08‰ for $\delta^{30}Si$ (2SD) and ±0.04‰ for $\delta^{29}Si$ (2SD). Long term reproducibility

205 of reference standards Diatomite and LMG08 (sponge) are reported as +1.22 ±0.15‰ and -3.45

206 ±0.14‰ (2SD) respectively. Mass dependent fractionation is demonstrated by a three-isotope plot of

207 all samples analysed during the study (Supplementary Fig. 2) with a gradient of 0.5118 (Reynolds et

208 al., 2007).

209

210 Sediment samples for $\delta^{30}ASi$ composition were prepared by adding 1ml 0.2M NaOH per 0.1mg ASi

211 and heating at 100°C for 1 hour. Samples were diluted and acidified with 8N HNO_3 and filtered

212 through 0.22µm PES syringe filters. Bulk bedrock samples were processed using alkaline fusion

213 (Georg et al., 2006) and the full procedure is detailed in Hawkings et al. (2018). Briefly, coarse,

214 unsorted debris were crushed and ground to form a fine powder using a planetary ball mill (Fritsch

215 Planetary Mono Mill Pulverisette 6). Debris was collected in front of the portal at LG and an ice cave

216 into the front of KS. Samples were then furnaced at 730°C with a NaOH pellet (approximately

217 200mg), diluted with MQ and acidified with 8N HNO_3 once cool. Water samples were prepared for

218 $\delta^{30}DSi$ by preconcentrating the samples via evaporation to approximately 2ml sample, ensuring 2ppm

219 of Si for analysis. All samples were then added to pre-cleaned BioRad exchange resin (AG50W-X12)

220 columns and eluted with MQ water (Georg et al., 2006).

221

3. Results

3.1 Defining periods of the melt seasons at KS and LG

224 We categorise the melt season into three parts at KS, following Dubnick et al. (2017); Early Season,

225 Transition Period and Late Season. These categories are defined by distinct changes in the proglacial

226 river hydrochemistry. The Early Season is defined by low discharge and a lack of relationship

227   between solutes, which is unlikely to reflect a subglacial signal. The Transition Period likely reflects

228   the time when the subglacial system became hydrologically connected and the bulk meltwaters

229   included a subglacially stored contribution (Hawkings et al., 2016; Dubnick et al., 2017). This period

230   includes a "Spring Event", which is a time of high glacier velocity, associated with increases in

231   subglacial water pressure discharge, suspended sediment and the divalent to monovalent cation ratio

232   (Dubnick et al., 2017, Mair et al., 2004; Fig. 2). The Late Season had a bulk melt water signature that

233   was distinct from the other periods analysed and is more similar to Alpine glacier geochemistry

234   (Tranter et al., 2002, Tranter and Wadham., 2014).

235   We also categorise the melt season at LG into Early Season and Late Season, defined by differences

236   in the hydrochemical data, with the transition being the first outburst event of the melt season. After

237   this outburst event, the hydrochemistry of the meltwaters shifts towards those indicative of silicate

238   mineral dissolution, as longer residence time waters are flushed.

239   **3.2 Dissolved major ions, DSi and δ^{30}DSi**

240   The ratio of ($Ca^{2+}+Mg^{2+}$) to (Na^++K^+) (divalent to monovalent cations, reported hereafter as D:M) has

241   traditionally been used to indicate the amount of silicate weathering in relation to carbonate

242   weathering (Tranter et al., 2002; Wadham et al., 2010). Elevated monovalent ion concentrations in

243   relation to divalent concentrations are associated with enhanced silicate mineral weathering. The

244   dissolved ion composition of glacial runoff from the two catchments changed significantly with

245   seasonal evolution of the subglacial drainage system (Fig. 3). The discharge-weighted mean (Qwt)

246   D:M (μeq L^{-1} : μeq L^{-1}) at LG was 1.36 compared to 6.91 at KS, with the D:M decreasing at LG as the

247   melt season progressed, from 5.18 to 1.44, compared to an increase in the D:M of a smaller magnitude

248   at KS (6.57 to 7.72, Fig. 3). Ca^{2+} was the dominant cation in KS over the entire melt season, consistent

249   with previously documented meltwaters from Alpine and Polar glaciers. However, there was a shift

250   from Ca^{2+} to Na^+ as the dominant cation as the melt season progressed at LG (Ca/Na molar ratios

251   started at 3.23 and decreased to 0.56 during outburst events, Fig. 4).

252   DSi concentrations in LG meltwaters decreased as the season progressed due to dilution from

253   supraglacial meltwaters (56.9μM to 9.21μM). The discharge weighted mean DSi concentration was

254   20.8 μM, similar to previously reported concentrations (Hindshaw et al., 2014; Hawkings et al., 2017).

255   KS had a slightly higher discharge weighted mean DSi of 22.2 μM, with a range of 14.8 μM to 41.8

256   μM. Concentrations also decreased as the subglacial hydrological drainage system developed from

257   inefficient to efficient drainage pathways (Supplementary Table 3 and 4).

258   There was a substantial decline in δ^{30}DSi at LG as the melt season progressed and the subglacial

259   system became hydrologically connected, with drainage of more isolated regions of the bed further up

260   catchment (Fig. 5d). The discharge weighted mean value of δ^{30}DSi at LG (-0.25 ± 0.12‰) was lighter

261   than the previous riverine average δ^{30}DSi composition (+1.25‰, Frings et al., 2016), and studies of

262 glacially fed rivers in Iceland (+0.17 ± 0.18‰, Opfergelt et al., 2013). The lightest values measured at

263 LG are more comparable to long residence time groundwaters (up to -1.42‰, Georg et al., 2009). KS

264 had a higher $\delta^{30}DSi$, with a discharge weighted mean of +0.41 ± 0.10‰, although this value is also

265 below the average riverine silicon isotope composition (Frings et al., 2016). The $\delta^{30}DSi$ at KS also

266 declined after the connection of the subglacial hydrological system ("Spring Event", Hawkings et al.,

267 2016, Mair et al. 2004) but the decline was not as substantial as that seen at LG (Fig. 5c).

268 **3.3 Saturation Indices**

269 Bulk meltwaters in both catchments were highly undersaturated with respect to ASi throughout the

270 melt season (LG SI_{ASi} = -1.04 to -1.85 and KS SI_{ASi} = -1.12 to -1.73). The lightest $\delta^{30}DSi$ composition

271 occurred when the proglacial river was most undersaturated with respect to ASi at both catchments

272 (Supplementary Fig. 3).

273 **3.4 Bedrock, SPM, ASi concentration and $\delta^{30}ASi$.**

274 Suspended particulate matter (SPM) concentrations in bulk meltwaters generally increased over time

275 in both catchments, as increasing amounts of sediment were entrained subglacially (Fig. 2). LG ASi

276 and SPM concentrations were significantly higher than KS (Table 1), with peak SPM coinciding with

277 subglacial outburst events (Hawkings et al. 2016, Fig. 2). Particles at LG also had a higher relative

278 proportion of extractable ASi, contributing to the elevated ASi concentrations (LG Qwt mean =

279 0.73wt%, compared to KS Qwt mean = 0.23wt%). However, KS has a higher specific discharge than

280 LG, so the yield of Si per km^2 is higher at KS. We estimate a mean annual ASi yield of 1.75 x 10^4 kg

281 km^{-2} from KS (Day 128 - 221) compared to an estimated mean yield of 1.24 x 10^4 kg km^{-2} from LG

282 (Day 135 – 210).

283 The $\delta^{30}ASi$ composition of SPM in bulk runoff was lighter at KS compared to LG, with little variation

284 at either site over the monitoring period (discharge weighted mean of -0.47 ± 0.06‰ compared to -

285 0.22 ± 0.06‰, Fig. 5). These values were lower than the local bedrock (KS -0.18 ± 0.06‰, LG 0.00 ±

286 0.07‰) and bulk suspended sediment (KS -0.32 ± 0.12‰, LG -0.09 ± 0.07‰).

287 **4. Discussion**

288 **4.1 Conceptual model of subglacial hydrology**

289 Differences in drainage system characteristics of glaciers at different spatial scale may result in

290 contrasting chemical weathering environments and water export mechanisms (Wadham et al., 2010;

291 Graly et al., 2014). Subglacial drainage systems of GrIS catchments likely include hydrological

292 elements that exist for the majority of the year and those that develop over time and shut down during

293 winter (Dubnick et al., 2017). The progression of the melt season is accompanied by an evolution

294 from slow-inefficient distributed to efficient (and potentially channelised) drainage systems as more

295 supraglacial meltwater reaches the bed (Bartholomew et al., 2011). Previous studies have

296 demonstrated that the seasonal evolution of subglacial hydrology impacts nutrient export dynamics

297 via the connection of chemically distinct, solute sources at the glacier bed (Bartholomew et al., 2011;

298 Bhatia et al., 2013; Hawkings et al., 2016; Dubnick et al., 2017; Kohler et al., 2017). LG has a

299 hydrologically active catchment of ~600km^2, is 80km long and has inland ice of low topography,

300 favouring the formation of large supraglacial lakes (often ~ kms in diameter, Hoffman et al., 2011).

301 These supraglacial lakes can drain rapidly (<2hours) through moulins to the glacier bed as a result of

302 hydrofracturing (Das et al., 2008; Bartholomew et al., 2011). Such drainage events can result in

303 outburst events being recorded in the proglacial hydrochemical records (Bartholomew et al., 2011;

304 Hawkings et al., 2015). Proglacial river discharge, suspended sediment and electrical conductivity

305 rapidly rise (Bartholomew et al., 2011, Hawkings et al., 2016; Fig. 2), as subglacially stored waters

306 and sediment become hydrologically connected and flushed downstream by incoming supraglacial

307 water (Bartholomew et al., 2011; Cowton et al., 2012; Chandler et al., 2013). Subglacial hydrological

308 evolution from inefficient to efficient drainage at the bed progresses from marginal to inland locations,

309 with artificial tracer work showing efficient drainage existing up to 40km from the margin by late July

310 (Chandler et al., 2013). This evolution is further supported by the seasonal progression of the ^{14}C age

311 of exported POC at LG (Kohler et al., 2017). The inland progression of the subglacial system could

312 mean that increasingly isolated meltwaters drain from the bed, since the interval between basal

313 flushing events via supraglacial lake drainage or moulins is longer in more inland locations

314 (potentially 10 months) compared to marginal locations (Harper and Humphrey, 1995). Residence

315 time differences between marginal and the most isolated inland waters are therefore likely to exist,

316 especially if similar regions of the bed are flushed annually (Fig. 6), with implications for weathering

317 and redissolution processes.

318 KS is only ~16km in length and there is comparatively little altitudinal difference from snout to the

319 top of the ablation area. Supraglacial lakes do not form at KS, thus some more isolated parts of the

320 bed may not be annually flushed by surface-to-bed water flow. The subglacial drainage system

321 development at KS is driven entirely by the progression of the snowline and the consequent opening

322 of new moulins and crevasses for surface to bed water flow, similar to smaller Arctic and Alpine

323 glaciers. Thus, the subglacial drainage system develops from inefficient distributed drainage, where

324 water follows a tortuous flow path, to an efficient, channelised system as the ablation season

325 progresses and meltwater inputs increase (Fig. 6, Tranter et al., 2002, Nienow et al., 2014). The

326 absence of supraglacial lake drainage and the smaller catchment size will shorten average residence

327 times of water emerging as bulk runoff. Any seasonal variation in subglacial water residence times is

328 likely on the order of weeks rather than months. We propose that the full length of KS could be

329 compared with the evolution of the first 10-20km of subglacial hydrology at LG prior to the onset of

330 outburst events, as demonstrated by the relationship between discharge and δ^{30}DSi (Fig. 5b). As there

331   is a limited input of long residence time stored water with differing geochemical composition at KS,

332   the chemical composition of the proglacial stream reflects a carbonate dominated weathering regime

333   (Tranter et al., 2002).

4.2 Differences in weathering regimes

335   Glacier size is hypothesised to have a major impact on chemical weathering via its influence upon

336   hydrological flow path length, and hence water residence times (Wadham et al., 2010). Our data show

337   clear differences in the major ion composition of bulk meltwaters draining from the study glacial

338   catchments (Figs. 3 and 7), indicating contrasting subglacial chemical weathering regimes. In larger

339   catchments silicate mineral dissolution is enhanced, as subglacially stored meltwaters reach saturation

340   with respect to calcite, due to the long residence times and subglacial isolation (Wadham et al., 2010;

341   Hawkings et al., 2016). Carbonate hydrolysis was previously believed to dominate over carbonation

342   in subglacial environments, due to the limited atmospheric connectivity, resulting in enhanced

343   concentration of divalent ions in meltwaters ($Ca^{2+}+Mg^{2+}$; Equation 2, Tranter et al., 2002). By

344   comparison, silicate hydrolysis results in elevated concentrations of monovalent ions ($Ka^{+}+Na^{+}$;

345   Equation 3, Tranter and Wadham, 2014).

346   <u>Leverett Glacier</u>

347   At LG, the progressive evolution in the D:M ratio is consistent with a shift towards silicate dominated

348   mineral weathering as the melt season progresses (Fig. 3). This trend in D:M is also consistent with

349   the Na-normalised molar ratios, which can be used to compare the hydrochemical signature to silicate

350   and carbonate endmembers in mixing diagrams (Gaillardet et al., 1999). Fig. 4 shows the evolution of

351   the LG towards the silicate endmember as the melt season progresses, with the outburst events lying

352   closest to this endmember. This suggests that isolated meltwaters characterised by long residence

353   times become hydrologically connected to a fast, efficient drainage systems and are exported to the

354   ice margin.

355   Subglacial meltwaters in inland regions may only be flushed by surface melt (e.g. via lake drainage

356   and moulins) after ~10 months when the snowline retreats this far from the ice margin and inland

357   hydrological systems become connected. During the intervening period, these subglacial meltwaters

358   are inferred to undergo enhanced silicate dissolution (Wadham et al., 2010; Chandler et al., 2013;

359   Graly et al., 2014). Hydrolysis of silicates also increases the pH within subglacial waters (Equations 2

360   and 3, Fig. 2), and these higher pH conditions further enhance the dissolution of aluminosilicate

361   minerals (Georg et al., 2009; Tranter and Wadham, 2014). Evolution towards low D:M ratios, and

362   elevated pH is particularly pronounced from Day 170 onwards in 2015 at LG after the first subglacial

363   outburst event (Q_{wt} pH after first outburst event 8.71, Fig. 2).

364 Coupled carbonate dissolution and sulphide oxidation is a more important process, during the Early

365 Season at LG. This importance is illustrated by gradients of $Ca^{2+}+Mg^{2+}$ versus SO_4^{2-} (Fig. 7a) and of

366 $Ca^{2+}+Mg^{2+}$ versus HCO_3^- (Fig. 7b) close to 2 (1.93 and 1.50 respectively, Tranter et al., 2002), which

367 closely resemble molar equivalent ratios of 2:1 for $Ca^{2+}+Mg^{2+}$ and SO_4^{2-}, and $Ca^{2+}+Mg^{2+}$ and HCO_3,

368 according to Equation 5. These findings are similar to those found by Graly et al. (2017), but are not

369 seen in a study which focused upon the middle to late part of the melt season at LG (Hindshaw et al.,

370 2014). We find higher concentrations of SO_4^{2-} in 2015 during the Early Season when discharge was

371 lower (Supplementary Fig. 4), which we can attribute to sulphide oxidation, highlighting the

372 importance of categorising the development of the melt season due to potentially large seasonal

373 differences. Furthermore, during the Early Season, the sulphate mass fraction (SMF, Equation 6) is

374 higher than later in the season (Supplementary Fig. 5), indicating a larger proportion of protons result

375 from sulphide oxidation. However, a SMF of <0.5 throughout the melt season indicates carbonation is

376 overall more important that sulphide oxidation as a proton supplier.

377 Following the first outburst event (Late Season), the gradients of $Ca^{2+}+Mg^{2+}$ v SO_4^{2-} and $Ca^{2+}+Mg^{2+}$

378 v HCO_3^- became shallower ($Ca^{2+}+Mg^{2+}$: SO_4^{2-} = 1.50:1, $Ca^{2+}+Mg^{2+}$: HCO_3^- = 0.79:1). The SMF also

379 decreases (~0.45 to ~0.25), indicating protons are largely provided from carbonation reactions. It is

380 likely that silicate dissolution via hydrolysis and carbonation is occurring in the Late Season at LG

381 (Wadham et al., 2010), especially when considering the concomitant increase in the gradient of the

382 lines of best fit for associations between HCO_3^- and SO_4^{2-} (Fig. 7c and embedded Table) from Early to

383 Late season at LG (0.96 to 1.17). Carbonation of silicates and carbonates consumes CO_2 in solution

384 and result in formation of HCO_3^-, which, combined with silicate hydrolysis, also helps to explain the

385 increasing pH as the melt season progresses. We expect that this increase in pH is the result of

386 increased hydrolysis and carbonation of silicates, due to the decline of $Ca^{2+}+Mg^{2+}$: HCO_3^- ratios as the

387 season progresses, indicating that the addition of HCO_3^- is occurring in the absence of $Ca^{2+}+Mg^{2+}$.

388 The meltwater geochemistry therefore suggests that LG begins as a system with the imprint of

389 sulphide oxidation coupled to carbonate dissolution (SMF = ~0.45, Equation 5). As the season

390 progresses and more isolated waters are exported, there is an increased importance of silicate

391 weathering linked to carbonation reactions (SMF = ~0.2).

392 <u>Kiattuut Sermiat</u>

393 Our conceptual model of the hydrology at KS leads to predictions of a relatively consistent subglacial

394 weathering regime once an efficient drainage system has developed. The source of solute in the

395 meltwaters at KS appears fairly consistent over the melt season. D:M ratio and mixing diagrams at KS

396 indicates that the system is dominated by carbonate weathering (Figs. 3, 4; also see Dubnick et al.

397 2017). We can use the ionic ratios to interrogate these relationships further and assess differences

398 between Early Season, Transition Period and Late Season.

399 During the Early Season at KS there is no significant relationships between $Ca^{2+}+Mg^{2+}$ and HCO_3^-

400 versus SO_4^{2-}. We would expect the higher SO_4^{2-} concentrations to be a result of sulphide oxidation.

401 Sulphide oxidation would usually be coupled with carbonate dissolution in glacial systems, which

402 should be reflected in molar equivalent ratios (Equation 5). However, the discharge is low at this time,

403 so it is likely that the proglacial river reflects groundwaters diluted with some snowmelt and/or

404 precipitation. Groundwater flow may be torturous, impacting upon the ionic ratios, and it is also likely

405 that these waters are more affected by atmospheric deposition than later in the season when discharge

406 is much greater (Bhatia et al., 2013). In the Early Season there are also longer turnover times of lake

407 water due to the lower discharge entering the lake, which results in slower flushing of system

408 (Supplementary Fig. 1).

409 It is during the Transition Period that the gradients for all the major ion relationships most closely

410 match those during the Early Season at LG (Fig. 7). There was an increase of HCO_3^- and $Ca^{2+}+Mg^{2+}$

411 in relation to SO_4^{2-} (Fig. 7a and 7c), which could be evidence of the connection of the subglacial

412 system to the proglacial hydrological system. As the dissolution of freshly comminuted glacial

413 sediments preferentially release HCO_3^- and $(Ca^{2+}+Mg^{2+})$ (via hydrolysis of trace carbonates), it would

414 be expected that the HCO_3^- and $Ca^{2+}+Mg^{2+}$ ratios with respect to SO_4^{2-} would increase. The elevated

415 HCO_3^- could also result from the microbial oxidation of organic carbon (Wadham et al., 2010). The

416 higher intercepts of HCO_3^- v SO_4^{2-}, and $(Ca^{2+}+Mg^{2+})$ v SO_4^{2-} compared to LG, suggest rapid

417 acquisition of (Ca^{2+}, Mg^{2+}) and HCO_3^- in relation to SO_4^{2-}, potentially due to carbonate hydrolysis.

418 Also, during the Transition Period, the $(Ca^{2+}+Mg^{2+})$: HCO_3 ratio increased to 1.50 (Fig. 7b), and the

419 SMF increased to ~0.18 (Supplementary Fig. 5). Collectively, these observations indicate some

420 influence from carbonate dissolution coupled to sulphide oxidation (Equation 5), similar to the Early

421 Season meltwaters at LG.

422 We see a prevalence of carbonate over silicate weathering during the Late Season at KS, providing

423 evidence of continuous availability of carbonate minerals within the subglacial system and a lack of

424 calcite saturation. Relationships close to 1:1 for $(Ca^{2+}+Mg^{2+})$: HCO_3 (Fig. 7b) show that carbonation

425 of carbonates and carbonate hydrolysis are the dominate weathering reactions throughout the melt

426 season, as a 1:1 ratio is expected from Equation 2.

427 The values measured at KS are similar to bulk meltwaters of Alpine glaciers studied, although the

428 SO_4^{2-} concentrations in the outflow from KS are lower (Tranter et al., 2002). The overall major ion

429 relationships indicate a shift from carbonate hydrolysis (Equation 2) and coupled carbonate

430 dissolution-sulphide oxidation (Equation 5) to carbonation of carbonates as the melt season progresses,

431 with little evidence of enhanced silicate weathering.

432 **4.3 Catchment hydrology as a driver of $\delta^{30}DSi$ seasonal variability**

433   By combining our conceptual model of subglacial hydrology at LG and KS with the observed major

434   ion ratio chemistry, we can begin to understand the geochemical drivers behind variations in $\delta^{30}Si$

435   composition of the meltwaters in each catchment. An increased predominance of silicate dissolution

436   as the melt season progresses at LG should theoretically result in higher $\delta^{30}DSi$, as silicate weathering

437   and the formation of secondary weathering products preferentially incorporate the lighter isotopes into

438   the newly formed solid (De La Rocha et al., 2000; Frings et al., 2016). While this pattern is observed

439   in non-glacial regimes, the lowest $\delta^{30}DSi$ values measured at LG coincided with the most pronounced

440   silicate weathering signals, and likely, by association, the longest residence time waters. We

441   hypothesise that the low $\delta^{30}DSi$ values measured at LG after Day 170 reflect the dissolution of

442   isotopically light ASi and secondary weathering products in subglacially stored waters and/or the

443   dissolution of isotopically light fresh mineral surface layers formed by enhanced physical weathering

444   (Hawkings et al., 2018). As the melt season progressed, the hydrologically active part of the

445   catchment retreated further inland and more isolated subglacial waters became hydrologically

446   connected (Hawkings et al., 2015), resulting in decreasing $\delta^{30}DSi$ (Fig. 5b) and D:M ratios as

447   discharge rose (Fig. 5a). The declining D:M ratios indicate a move to increasingly dominant silicate

448   weathering and redissolution of secondary weathering products from the more isolated subglacial

449   system or longer residence time waters, resulting in more dissolution of these finely ground

450   weathering crusts, which results in the lowering of the $\delta^{30}DSi$ composition.

451   Some decline in $\delta^{30}DSi$ also occurred during the Transition Period at KS (Fig. 5c), which was likely

452   linked to the opening of subglacial hydrological pathways and flushing of a formerly distributed

453   drainage system. We would expect redissolution of secondary weathering products to occur at KS due

454   to the high pH and the undersaturation of ASi (Crompton et al., 2015, Supplementary Fig. 3).

455   However, $\delta^{30}DSi$ composition at KS is consistently higher than $\delta^{30}ASi$ and bedrock values (Fig. 4d),

456   indicating that the $\delta^{30}DSi$ exported is a result of fractionation due to net secondary weathering product

457   formation (Crompton et al., 2015). We hypothesis that the shorter residence times beneath KS

458   compared to LG reduce the potential for redissolution of secondary weathering products to occur. It

459   is more likely that there are fewer inland regions that remain isolated at KS, and the supraglacial

460   waters are routed more efficiently through the subglacial system.

461   KS and LG have broadly similar bedrock compositions (Hawkings et al., 2016), with any differences

462   unlikely to have a major impact on the overall $\delta^{30}Si$ composition of the measured bulk bedrock

463   (Savage et al., 2010). The intrusive rocks of the Julianhåb batholith and the Gardar Province at KS

464   would be expected to have a limited range in $\delta^{30}Si$ values due to minimal isotope fractionation during

465   high temperature mantle processes (Savage et al., 2010; Savage et al., 2014). Therefore, our

466   measurements of crushed proglacial rock debris for both catchments are in good agreement with the

467   published range of values measured in West Greenland (Andre et al., 2006). The measured mean

468   bedrock values of $\delta^{30}Si$ at KS are lighter compared to LG (-0.18 ± 0.06‰ compared to 0.00 ±0.07‰),

469   making them more comparable to values for bulk silicates on the Earth's surface (-0.29±0.08‰,

470   Savage et al. 2010). The heavier δ^{30}Si composition measured at LG could be an artefact of sampling

471   bedrock with a weathering crust, rather than pristine samples. However, basalts have a lower isotopic

472   composition (-0.3‰ to -0.2‰, Georg et al., 2007; Chemtob et al., 2015), so it is possible KS bedrock

473   is isotopically lighter, as a result of basaltic intrusions. Nevertheless, we attribute variations in silicon

474   isotope composition of SPM ASi to be largely a result of weathering processes at the glacier bed. The

475   isotopic fractionations caused by weathering conditions has been shown to be much greater than any

476   variations in crustal samples, despite often significant differences in compositions (Ziegler et al., 2005;

477   Savage et al., 2010; Savage et al., 2013).

478   Neither catchment showed a seasonal trend in SPM δ^{30}ASi, which exhibited a constant offset towards

479   lower values compared to our bulk bedrock measurements (˜0.1 to 0.2‰; Fig. 5c, d). The offset could

480   be the result of fractionation induced precipitation reactions, weathering of silicate rocks,

481   comminution of particles, or a combination of all three (Andre et al., 2006; Chemtob et al., 2015). The

482   precipitation of ASi at low temperatures results in the preferential uptake of ^{28}Si into the solid phase

483   (e.g. Geiler et al. 2014). High resolution transmission electron microscope photomicrographs of ASi

484   in SPM show it to be associated with edges of particles and with elements such as Al and Fe,

485   suggesting it potentially forms as a result of aluminosilicate mineral weathering (Hellmann et al.,

486   2012; Hawkings et al., 2017). The presence of ASi with elevated Al/Si ratios indicates that it would

487   also be enriched in ^{28}Si, based on prior low temperature laboratory experiments (Oelze et al., 2015).

488   However, the offset in SPM δ^{30}ASi from the bedrock measurements could also be linked to physical

489   grinding, which has been demonstrated to result in the formation of reactive amorphous surface layers

490   (Lin and Somasundaran, 1972; Hawkings et al., 2017). ASi formed in this way is likely to be

491   characterised by isotopically light compositions as it is derived from the alteration of a freshly crushed

492   outer mineral layer, enriched in ^{28}Si, due to kinetic fractionation (Zielger et al., 2005). All three

493   processes result in ASi enriched in ^{28}Si, so our current data is unable to infer which of these is most

494   important as ASi from both catchments are lighter than bedrock values across the season.

4.4 Understanding the Isotopic Mass Imbalance

496   The interpretations presented above highlight a potential mass imbalance that arises because the

497   subglacial waters export both DSi and ASi that is isotopically lighter than bedrock values at LG. In

498   addition to this, when the δ^{30}DSi and δ^{30}ASi compositions at LG are summed, considering the relative

499   contributions of both, the total δ^{30}Si is consistently lighter than the measured bedrock across the melt

500   season. Whilst we have sampled the majority of the melt season at LG (>60%), we did not continue

501   sampling until the shutdown of the subglacial system. Therefore, we have carried out a simple mass

502   balance calculation to ensure the mass imbalance seen at LG is not simply an artefact of the

503   unmonitored part of the season (Supplementary Table 5). Whilst we do not have geochemical data

504   past Day 210, we have a continuous discharge (Q) record until much later in the season. From this

505   record we calculated the proportion of the measured discharge compared to the total discharge. We

506   assumed that DSi concentrations were similar to the discharge weighted mean from the measured

507   period. As the δ^{30}ASi composition was relatively constant across the measured period, this trend

508   would likely continue into the latter stages of the season. We estimate the δ^{30}Si composition of the

509   unmeasured DSi required to ensure the total Si exported had a δ^{30}Si composition that matched the

510   bulk bedrock composition. The overall δ^{30}Si composition after the sampling period would need to be

511   +0.44‰, with a δ^{30}DSi composition of +2.22‰, in order to balance the δ^{30}Si composition over the

512   rest of the melt season. The aim of this simple calculation was to demonstrate whether the mass

513   imbalance could be realistically resolved by only considering the latter stages of the melt season,

514   which we were unable to sample. A δ^{30}DSi composition of +2.22‰ is likely unrealistic, considering

515   the range of values measured over the rest of the season are significantly lighter. It is therefore likely

516   the subglacial processes are driving the mass imbalance seen at LG.

517

518   One hypothesis to explain this mass imbalance is that the continuing light δ^{30}DSi values of bulk

519   meltwaters reflect physical erosion processes. High physical erosion of bedrock under the GrIS results

520   in the formation of fresh finely ground rock flour, with very high surface areas (Cowton et al., 2012;

521   Telling et al., 2015; Hawkings et al., 2016; Nienow et al., 2017). Published dissolution experiments

522   have shown there is a preferential dissolution of [28]Si from the fresh mineral surface, as a result of

523   kinetic fractionation (Ziegler et al., 2005). Therefore, we expect that the freshly crushed subglacial

524   minerals to result in delivery of dissolved silicon enriched in [28]Si. The high pH and under saturation of

525   waters with respect to ASi subsequently promotes the outer amorphous mineral layers to undergo

526   further dissolution, resulting in the export of light δ^{30}DSi. The higher δ^{30}DSi composition at the

527   beginning of the season reflects the weathering environment at marginal areas of the ice sheet. These

528   areas are accessed more regularly by surface melt, with efficient hydrological drainage for longer

529   parts of the season (Chandler et al., 2013), and with potentially less active grinding of bedrock (as

530   demonstrated by lower suspended sediment concentrations during the Early Season). As the melt

531   season progresses, more isolated inland regions of the bed are accessed, where dissolution has

532   occurred over longer time periods and where physical erosion is enhanced, potentially evidenced by

533   the linear relationship between increasing SPM concentrations and decreasing δ^{30}DSi exported from

534   LG (Supplementary Fig. 6). Hence, the δ^{30}DSi of meltwaters exported is lower. By comparison, SPM

535   concentrations exported from KS are consistently lower. This could be a result of some settling in the

536   proglacial lake, but we believe it is more likely to result from lower rates of physical erosion in this

537   smaller catchment. We therefore hypothesise that higher physical erosion rates and longer residence

538   times in larger catchments (Wadham et al., 2010, Hawkings et al., 2016), help to explain the

539   differences in the δ^{30}Si composition of meltwaters from LG and KS.

540   To quantitatively assess if this hypothesis is realistic, we have modelled the proportion of DSi that

541   would need to result from the dissolution of ASi associated with SPM, assuming complete

542   dissolution, when considering the δ^{30}Si composition of the measured DSi and corresponding

543   endmembers (Equation 7). Our model was based on a range of fractionation factors for the initial

544   formation of ASi (ϵ) from the alteration of bedrock, as low temperature fractionation processes are

545   still poorly understood (Geilert et al., 2014; Frings et al., 2016). An open system was chosen, rather

546   than using Rayleigh fractionation, as we do not expect a finite pool of Si within the subglacial system

547   in the timescales we are considering.

548

549   The subglacial environment is complex; therefore, so we have simplified our model by assuming

550   overall fractionation during bedrock alteration to form ASi is similar to that observed during low

551   temperature ASi precipitation from solution with ϵ ranging from -2 ‰ to -5 ‰. Extrapolation from

552   experiments by Geilert et al. (2014) produces a fractionation factor of -2.34‰ at 0°C. However their

553   conclusions indicate that the fractionation factor at low temperatures is system dependent, due to

554   differences in fractionation based on external factors such as saturation state and surface area. Oelze

555   et al. (2015) found a fractionation factor of -5‰ for initial stages of experiments with high Al/Si

556   ratios, which could simulate subglacial conditions considering the potential formation of ASi through

557   aluminosilicate weathering (Hawkings et al., 2017). We use the first δ^{30}DSi value measured in the

558   Early Season at KS and a value measured at the subglacial portal in the Early Season at LG as the

559   initial δ^{30}DSi endmember in the model. The δ^{30}ASi endmember value is calculated by subtracting the

560   chosen fractionation factor from the δ^{30}Si composition of the bulk rock for each catchment.

561

562   In our modelled scenarios for LG we show that during outburst periods (and thus when δ^{30}DSi

563   composition is lightest), a maximum of 56% of the measured DSi results from ASi dissolution (Fig. 8).

564   This proportion equates to ~12μM of ASi compared to an overall ASi concentration of ~290μM

565   measured at the same timepoint, suggesting that even the maximum modelled values can be

566   considered reasonable due to the large ASi reservoir. Experimental data also suggest the most

567   negative ϵ values relate to solids formed rapidly and with unidirectional kinetic fractionation effects

568   (Oelze et al., 2015), which could also relate to these subglacial weathering crusts which are highly

569   reactive and would presumably undergo rapid dissolution. While all the modelled f_a values can be

570   considered realistic when converted to molar concentrations, we consider the lower values as more

571   representative of subglacial systems, considering the experimental data from Oelze et al. (2015).

572   Despite the lower ASi concentrations at KS, the modelled values can also be considered realistic for

573   this system. As we expect the ASi dissolution to be less important at KS compared to at LG, it follows

574   that we calculate lower proportions of ASi required to undergo dissolution in order to produce the

575   measured δ^{30}DSi. We would expect the DSi at KS to be a result of silicate dissolution, from

576 hydrolysis reactions, with the formation of clay minerals as a secondary weathering product

577 (Crompton, 2015), as evidenced by increasing pH and the heavier $\delta^{30}DSi$ when compared to LG.

578 An alternative hypothesis to explain the mass imbalance at LG requires a temporal offset between

579 weathering product formation and re-dissolution. For example, the isotopically light secondary

580 weathering products may be a pre-glacial feature formed in a past, warmer climatic regime,

581 sequestered by an advancing ice sheet under a cooler climate and were stored subglacially (Hawkings

582 et al., 2018). The presence of palaeosols (>2.7million years, Bierman et al. 2014) beneath the ice

583 sheet, which are exported in runoff, supports the notion that there are pre-glacial features present

584 (Lawson et al., 2014; Kohler et al., 2017). The high pH of LG meltwaters (up to 9.63),

585 undersaturation of waters with respect to ASi, and high ASi concentrations (Qwt mean 209μM after

586 Day 170), could result in the redissolution of these isotopically light amorphous secondary weathering

587 products when the isolated parts of the subglacial system become hydrologically connected

588 (Hawkings et al., 2018). Whilst this hypothesis provides explanation for the potential mass imbalance

589 and palaeosols are evidenced beneath ice sheets, it may be expected that this isotopically light source

590 of Si would get depleted over time and any enhanced weathering currently occurring *in-situ* would

591 result in heavier $\delta^{30}DSi$ exported in the meltwaters. Also, ASi measurements in the current proglacial

592 plain display very low concentrations (average 0.01wt%, Supplementary Table 6), suggesting these

593 amorphous phases are not currently being formed in the current proglacial environment, or have been

594 stripped away or aged. Therefore, whilst this hypothesis has potential to provide explanation for light

595 $\delta^{30}DSi$ compositions in glacial meltwaters, our data suggests our first hypothesis focusing on physical

596 erosion is currently the most likely scenario.

4.5 Implications and Conclusions

598 The two Greenland Ice Sheet (GrIS) catchments have different subglacial weathering regimes

599 primarily driven by subglacial hydrology. These weathering regimes appear related to water residence

600 time and therefore catchment size. Kiattuut Sermiat (KS) was dominated by carbonate hydrolysis,

601 whereas a predominance of silicate mineral weathering occurred as the melt season progressed at

602 Leverett Glacier (LG). Subglacial silicate weathering results in the production of isotopically light

603 amorphous secondary weathering solid phases in both catchments, with heavier isotopes recorded in

604 the dissolved fraction during Early Season meltwater discharge. As the melt season progressed, long

605 residence time subglacial waters became connected to an efficient drainage system. The larger of the

606 two catchments in this study, LG, exhibited a marked decrease in $\delta^{30}DSi$ from 0.87 to -0.55‰, as

607 meltwater discharge rose, and the subglacial drainage system expanded inland, tapping increasingly

608 remote subglacial water pockets. We interpret this isotopic shift as evidence of increasing contribution

609 from silicate weathering products, including the dissolution of ASi and other secondary weathering

610 products, and leaching of freshly crushed rock surfaces. The smaller catchment, KS, discharged

611   meltwaters with a δ^{30}DSi similar to smaller valley glaciers, with carbonate weathering the

612   predominant solute acquisition pathway.

613   Our results show that δ^{30}DSi and δ^{30}ASi can be used alongside major ion data to assess the degree of

614   silicate weathering, redissolution of weathering products and hydrological drainage characteristics in

615   glacial meltwaters. We postulate that access to meltwater present in subglacial drainage systems with

616   limited connection to an efficient drainage system will increase in the future, as snowlines retreat

617   further inland and melt increases under climatic warming (Hawkings et al., 2015). It is therefore likely

618   that the intensity of subglacial geochemical weathering and the composition of glacial waters entering

619   the ocean will be impacted. These findings are critical when attempting to estimate the fluxes of

620   nutrients from rapidly melting glaciated regions and their impact on elemental cycles, in the past (e.g.

621   during deglaciation events, Hawkings et al., 2018), present and future. The residence time of

622   subglacial waters will have an influence on the weathering reactions occurring, and therefore the

623   fluxes of key nutrients (Fe, P and Si) exported from glacial systems (Stevenson et al., 2017). More

624   robust estimation of Si fluxes and the δ^{30}Si composition of exported waters from the GrIS requires full

625   consideration and further study of catchment size, hydrological development, weathering regime, and

626   other processes within the complex subglacial system. The degree of silicate weathering in glaciated

627   regions may be much higher than previously thought, considering that it is the larger catchments that

628   discharge the majority of meltwater into the ocean from the GrIS and AIS. The quantity of meltwater

629   delivered Si from ice sheets and its isotopic composition should therefore be considered when

630   calculating global silicon budgets.

631   **Acknowledgements**

644 References
645

646 Andre L., Cardinal D., Alleman L. and Moorbath S. (2006) Silicon isotopes in ∼3.8 Ga West Greenland
647 rocks as clues to the Eoarchaean supracrustal Si cycle. *Earth and Planetary Science Letters* **245**, 162-
648 173.
649 Bartholomew I., Nienow P., Sole A., Mair D., Cowton T., Palmer S. and Wadham J. (2011) Supraglacial
650 forcing of subglacial drainage in the ablation zone of the Greenland ice sheet. *Geophysical Research*
651 *Letters* **38**.
652 Berner R.A. (2003) The long-term carbon cycle, fossil fuels and atmospheric composition. *Nature* **426**,
653 323.
654 Bhatia M.P., Das S.B., Xu L., Charette M.A., Wadham J.L. and Kujawinski E.B. (2013) Organic carbon
655 export from the Greenland ice sheet. *Geochim. Cosmochim. Acta* **109**, 329-344.
656 Bierman P.R., Corbett L.B., Graly J.A., Neumann T.A., Lini A., Crosby B.T. and Rood D.H. (2014)
657 Preservation of a Preglacial Landscape Under the Center of the Greenland Ice Sheet. *Science* **344**,
658 402-405.
659 Bouysse P. (2014) Geological Map of the World at 1: 35 000 000, 3rd Edition ed. CCGM-CGMW.
660 Cardinal D., Alleman L.Y., de Jong J., Ziegler K. and Andre L. (2003) Isotopic composition of silicon
661 measured by multicollector plasma source mass spectrometry in dry plasma mode. *Journal of*
662 *Analytical Atomic Spectrometry* **18**, 213-218.
663 Cardinal D., Gaillardet J., Hughes H.J., Opfergelt S. and André L. (2010) Contrasting silicon isotope
664 signatures in rivers from the Congo Basin and the specific behaviour of organic-rich waters.
665 *Geophysical Research Letters* **37**.
666 Chandler D.M., Wadham J.L., Lis G.P., Cowton T., Sole A., Bartholomew I., Telling J., Nienow P.,
667 Bagshaw E.B., Mair D., Vinen S. and Hubbard A. (2013) Evolution of the subglacial drainage system
668 beneath the Greenland Ice Sheet revealed by tracers. *Nature Geosci* **6**, 195-198.
669 Chemtob S.M., Rossman G.R., Young E.D., Ziegler K., Moynier F., Eiler J.M. and Hurowitz J.A. (2015)
670 Silicon isotope systematics of acidic weathering of fresh basalts, Kilauea Volcano, Hawai'i. *Geochim.*
671 *Cosmochim. Acta* **169**, 63-81.
672 Conley D.J. (1998) An interlaboratory comparison for the measurement of biogenic silica in
673 sediments. *Marine Chemistry* **63**, 39-48.
674 Cowton T., Nienow P., Bartholomew I., Sole A. and Mair D. (2012) Rapid erosion beneath the
675 Greenland ice sheet. *Geology* **40**, 343-346.
676 Crompton J.W., Flower, G. E., Kirste, D., Hagedorn, B., and Sharp, M. J. (2015) Clay mineral
677 precipitation and low silica in glacier meltwaters explored through reaction-path modelling. *Journal*
678 *of Glaciology* **61**, 1061-1078.
679 Das S.B., Joughin I., Behn M.D., Howat I.M., King M.A., Lizarralde D. and Bhatia M.P. (2008) Fracture
680 Propagation to the Base of the Greenland Ice Sheet During Supraglacial Lake Drainage. *Science* **320**,
681 778-781.
682 De La Rocha C.L., Brzezinski M., A. and DeNiro M.J. (2000) A first look at the distribution of the stable
683 isotopes of silicon in natural waters. *Geochim. Cosmochim. Acta* **64**, 2467-2477.
684 De la Rocha C.L., Brzezinski M.A. and DeNiro M.J. (1997) Fractionation of silicon isotopes by marine
685 diatoms during biogenic silica formation. *Geochim. Cosmochim. Acta* **61**, 5051-5056.
686 DeMaster D., J. (1981) The Supply and Accumulation of Silica in the Marine-Environment. *Geochim.*
687 *Cosmochim. Acta* **45**, 1715-1732.
688 Ding T., Wan D., Bai R., Zhang Z., Shen Y. and Meng R. (2005) Silicon isotope abundance ratios and
689 atomic weights of NBS-28 and other reference materials. *Geochim. Cosmochim. Acta* **69**, 5487-5494.
690 Ding T., Wan D., Wang C. and Zhang F. (2004) Silicon isotope compositions of dissolved silicon and
691 suspended matter in the Yangtze River, China. *Geochim. Cosmochim. Acta* **68**, 205-216.
692 Ding T.P., Gao J.F., Tian S.H., Wang H.B. and Li M. (2011) Silicon isotopic composition of dissolved
693 silicon and suspended particulate matter in the Yellow River, China, with implications for the global
694 silicon cycle. *Geochim. Cosmochim. Acta* **75**, 6672-6689.

695 Dubnick A., Kazemi S., Sharp M., Wadham J., Hawkings J., Beaton A. and Lanoil B. (2017) Hydrological
696 controls on glacially exported microbial assemblages. *Journal of Geophysical Research:*
697 *Biogeosciences* **122**, 1049-1061.
698 Escher A., Watt, W. S. (1976) Geology of Greenland, Grønlands Geologiske undersøgelse.
699 Fontorbe G., De La Rocha C.L., Chapman H.J. and Bickle M.J. (2013) The silicon isotopic composition
700 of the Ganges and its tributaries. *Earth and Planetary Science Letters* **381**, 21-30.
701 Frings P.J., Clymans W., Fontorbe G., De La Rocha C. and Conley D.J. (2016) The continental Si cycle
702 and its impact on the ocean Si isotope budget. *Chemical Geology* **425**, 12-36.
703 Gaillardet J., Dupré B., Louvat P. and Allègre C.J. (1999) Global silicate weathering and CO2
704 consumption rates deduced from the chemistry of large rivers. *Chemical Geology* **159**, 3-30.
705 Geilert S., Vroon P.Z., Roerdink D.L., Van Cappellen P. and van Bergen M.J. (2014) Silicon isotope
706 fractionation during abiotic silica precipitation at low temperatures: Inferences from flow-through
707 experiments. *Geochim. Cosmochim. Acta* **142**, 95-114.
708 Georg R.B., Reynolds B.C., Frank M. and Halliday A.N. (2006) New sample preparation techniques for
709 the determination of Si isotopic compositions using MC-ICPMS. *Chemical Geology* **235**, 95-104.
710 Georg R.B., Reynolds B.C., West A.J., Burton K.W. and Halliday A.N. (2007) Silicon isotope variations
711 accompanying basalt weathering in Iceland. *Earth and Planetary Science Letters* **261**, 476-490.
712 Georg R.B., Zhu C., Reynolds B.C. and Halliday A.N. (2009) Stable silicon isotopes of groundwater,
713 feldspars, and clay coatings in the Navajo Sandstone aquifer, Black Mesa, Arizona, USA. *Geochim.*
714 *Cosmochim. Acta* **73**, 2229-2241.
715 Graly J., Harrington J. and Humphrey N. (2017) Combined diurnal variations of discharge and
716 hydrochemistry of the Isunnguata Sermia outlet, Greenland Ice Sheet. *The Cryosphere* **11**, 1131-1140.
717 Graly J.A., Humphrey N.F., Landowski C.M. and Harper J.T. (2014) Chemical weathering under the
718 Greenland Ice Sheet. *Geology* **42**, 551-554.
719 Harper J.T. and Humphrey N.F. (1995) Borehole video analysis of a temperate glacier' englacial and
720 subglacial structure: Implications for glacier flow models. *Geology* **23**, 901-904.
721 Hawkings J., Wadham J., Tranter M., Telling J., Bagshaw E., Beaton A., Simmons S.-L., Chandler D.,
722 Tedstone A. and Nienow P. (2016) The Greenland Ice Sheet as a hot spot of phosphorus weathering
723 and export in the Arctic. *Global Biogeochemical Cycles* **30**, 191-210.
724 Hawkings J.R., Hatton J.E., Hendry K.R., de Souza G.F., Wadham J.L., Ivanovic R., Kohler T.J., Stibal M.,
725 Beaton A., Lamarche-Gagnon G., Tedstone A., Hain M.P., Bagshaw E., Pike J. and Tranter M. (2018)
726 The silicon cycle impacted by past ice sheets. *Nature Communications* **9**, 3210.
727 Hawkings J.R., Wadham J.L., Benning L.G., Hendry K.R., Tranter M., Tedstone A., Nienow P. and
728 Raiswell R. (2017) Ice sheets as a missing source of silica to the polar oceans. *Nature*
729 *Communications* **8**, 14198.
730 Hawkings J.R., Wadham J.L., Tranter M., Lawson E., Sole A., Cowton T., Tedstone A.J., Bartholomew I.,
731 Nienow P., Chandler D. and Telling J. (2015) The effect of warming climate on nutrient and solute
732 export from the Greenland Ice Sheet. *Geochemical Perspectives Letters*, 94-104.
733 Hellmann R., Wirth R., Daval D., Barnes J.-P., Penisson J.-M., Tisserand D., Epicier T., Florin B. and
734 Hervig R.L. (2012) Unifying natural and laboratory chemical weathering with interfacial dissolution–
735 reprecipitation: A study based on the nanometer-scale chemistry of fluid–silicate interfaces.
736 *Chemical Geology* **294-295**, 203-216.
737 Hendry K. and Robinson L.F. (2012) The relationship between silicon isotope fractionation in sponges
738 and silicic acid concentration.: Modern and core-top studies of biogenic opal. *Geochim. Cosmochim.*
739 *Acta* **81**, 1-12.
740 Henriksen N., Higgins, A. K., Kalsbeek, F., and Pulvertaft, T. C. R. (2009) Greenland From Archaean to
741 Quaternary Descriptive Text to the 1995 Geological Map of Greenland, 1:2 500 000, Geol. Surv. Den.
742 Greenl., Geological Survey of Denmark and Greenland, 2nd Edition ed, Copenhagen, pp. 9-116.
743 Hindshaw R.S., Rickli J., Leuthold J., Wadham J. and Bourdon B. (2014) Identifying weathering
744 sources and processes in an outlet glacier of the Greenland Ice Sheet using Ca and Sr isotope ratios.
745 *Geochim. Cosmochim. Acta* **145**, 50-71.

Hoffman M.J., Catania G.A., Neumann T.A., Andrews L.C. and Rumrill J.A. (2011) Links between acceleration, melting, and supraglacial lake drainage of the western Greenland Ice Sheet. *Journal of Geophysical Research: Earth Surface* **116**.

Hughes H.J., Delvigne C., Korntheuer M., de Jong J., André L. and Cardinal D. (2011) Controlling the mass bias introduced by anionic and organic matrices in silicon isotopic measurements by MC-ICP-MS. *Journal of Analytical Atomic Spectrometry* **26**, 1892.

Kohler T.J., Zarsky J.D., Yde J.C., Lamarche-Gagnon G., Hawkings J.R., Tedstone A.J., Wadham J.L., Box J.E., Beaton A.D. and Stibal M. (2017) Carbon dating reveals a seasonal progression in the source of particulate organic carbon exported from the Greenland Ice Sheet. *Geophysical Research Letters* **44**, 6209-6217.

Lawson E.C., Wadham J.L., Tranter M., Stibal M., Lis G.P., Butler C.E.H., Laybourn-Parry J., Nienow P., Chandler D. and Dewsbury P. (2014) Greenland Ice Sheet exports labile organic carbon to the Arctic oceans. *Biogeosciences* **11**, 4015-4028.

Lin I.J. and Somasundaran P. (1972) Alterations in properties of samples during their preparation by grinding. *Powder Technology* **6**, 171-179.

Mair D., Willis I., Fischer U.H., Hubbard B., Nienow P. and Hubbard A. (2004) Hydrological controls on patterns of surface, internal and basal motion during three "spring events": Haut Glacier d'Arolla, Switzerland. *Journal of Glaciology* **49**, 555-567.

Michaud A.B., Skidmore M.L., Mitchell A.C., Vick-Majors T.J., Barbante C., Turetta C., vanGelder W. and Priscu J.C. (2016) Solute sources and geochemical processes in Subglacial Lake Whillans, West Antarctica. *Geology* **44**, 347-350.

Nienow P. (2014) The plumbing of Greenland's ice. *Nature* **514**, 38.

Nienow P., Sharp M. and Willis I.C. (1998) Seasonal changes in the morphology of the subglacial drainage system, Haut Glacier d'Arolla, Switzerland. *Earth Surface Processes and Landforms* **23**, 825-843.

Nienow P.W., Sole A.J., Slater D.A. and Cowton T.R. (2017) Recent Advances in Our Understanding of the Role of Meltwater in the Greenland Ice Sheet System. *Current Climate Change Reports* **3**, 330-344.

Oelze M., von Blanckenburg F., Bouchez J., Hoellen D. and Dietzel M. (2015) The effect of Al on Si isotope fractionation investigated by silica precipitation experiments. *Chemical Geology* **397**, 94-105.

Opfergelt S., Burton K.W., Pogge von Strandmann P.A.E., Gislason S.R. and Halliday A.N. (2013) Riverine silicon isotope variations in glaciated basaltic terrains: Implications for the Si delivery to the ocean over glacial–interglacial intervals. *Earth and Planetary Science Letters* **369-370**, 211-219.

Reynolds B.C., Aggarwal J., André L., Baxter D., Beucher C., Brzezinski M.A., Engström E., Georg R.B., Land M., Leng M.J., Opfergelt S., Rodushkin I., Sloane H.J., van den Boorn S.H.J.M., Vroon P.Z. and Cardinal D. (2007) An inter-laboratory comparison of Si isotope reference materials. *Journal of Analytical Atomic Spectrometry* **22**, 561-568.

Sauer D., Saccone L., Conley D.J., Herrmann L. and Sommer M. (2006) Review of methodologies for extracting plant-available and amorphous Si from soils and aquatic sediments. *Biogeochemistry* **80**, 89-108.

Savage P.S., Georg R.B., Armytage R.M.G., Williams H.M. and Halliday A.N. (2010) Silicon isotope homogeneity in the mantle. *Earth and Planetary Science Letters* **295**, 139-146.

Savage P.S., Georg R.B., Williams H.M. and Halliday A.N. (2013) Silicon isotopes in granulite xenoliths: Insights into isotopic fractionation during igneous processes and the composition of the deep continental crust. *Earth and Planetary Science Letters* **365**, 221-231.

Stevenson E.I., Fantle M.S., Das S.B., Williams H.M. and Aciego S.M. (2017) The iron isotopic composition of subglacial streams draining the Greenland ice sheet. *Geochim. Cosmochim. Acta* **213**, 237-254.

Telling J., Boyd E.S., Bone N., Jones E.L., Tranter M., MacFarlane J.W., Martin P.G., Wadham J.L., Lamarche-Gagnon G., Skidmore M.L., Hamilton T.L., Hill E., Jackson M. and Hodgson D.A. (2015) Rock comminution as a source of hydrogen for subglacial ecosystems. *Nature Geoscience* **8**, 851.

797   Tranter M., Sharp M.J., Lamb H.R., Brown G.H., Hubbard B.P. and Willis I.C. (2002) Geochemical
798   weathering at the bed of Haut Glacier d'Arolla, Switzerland - A new model. *Hydrological Processes* **16**,
799   959-993.
800   Tranter M. and Wadham J.L. (2014) 7.5 - Geochemical Weathering in Glacial and Proglacial
801   Environments A2 - Holland, Heinrich D, in: Turekian, K.K. (Ed.), Treatise on Geochemistry (Second
802   Edition). Elsevier, Oxford, pp. 157-173.
803   Wadham J.L., Tranter M., Skidmore M., Hodson A.J., Priscu J., Lyons W.B., Sharp M., Wynn P. and
804   Jackson M. (2010) Biogeochemical weathering under ice: Size matters. *Global Biogeochemical Cycles*
805   **24**.
806   Walker J.C.G., Hays P.B. and Kasting J.F. (1981) A negative feedback mechanism for the long-term
807   stabilization of Earth's surface temperature. *Journal of Geophysical Research: Oceans* **86**, 9776-9782.
808   Yde J.C., Knudsen N.T., Hasholt B. and Mikkelsen A.B. (2014) Meltwater chemistry and solute export
809   from a Greenland Ice Sheet catchment, Watson River, West Greenland. *Journal of Hydrology* **519**,
810   2165-2179.
811   Ziegler K., Chadwick O.A., Brzezinski M.A. and Kelly E.F. (2005) Natural variations of δ30Si ratios
812   during progressive basalt weathering, Hawaiian Islands. *Geochim. Cosmochim. Acta* **69**, 4597-4610.
813   Ziegler K., Chadwick O.A., Kelly E.F. and Brzezinski M.A. (2002) The δ30Si values of soil weathering
814   profiles: Indicators of Si pathways at the lithosphere/hydro (bio) sphere interface. *Geochim.*
815   *Cosmochim. Acta* **66**, A881.

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817   **Table 1: Hydrological comparison of two studied catchments.** Qwt = discharge weighted mean,
818   D:M = divalent to monovalent ion ratio, DSi = Dissolved silicate, ASi = Amorphous silica.
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	Kiattuut Sermia (2013)	Leverett Glacier (2015)
Mean Q (m^3S^{-1})	22.80^+	85.35
Total Q (km^3)	0.22^+	1.45
Qwt Sus. Sediment (g L^{-1})	0.12^+	0.87
Qwt pH	9.09	8.63
Qwt EC (µS cm^{-1})	26.66^+	12.25
Qwt D:M (µeq)	6.91	1.36
Qwt DSi (µM)	22.18	20.76
Qwt ASi (µM)	9.87	205.78
Qwt δ^{30}DSi (‰)	0.41	-0.25
Qwt δ^{30}ASi (‰)	-0.47	-0.22
Bulk Rock δ^{30}Si (‰)	-0.18	0.00^+

820   [+]Data previously published by Hawkings et al. (2016).
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822   **Figure 1: Location of Kiattuut Sermiat and Leverett Glacier, from Hawkings et al. (2016)**. Water
823   samples were collected at the locations marked in black from proglacial streams, as in Lawson et al.
824   (2014) and Hawkings et al. (2016). Hydrological monitoring was completed at points of stable
825   bedrock (white markers).

826   **Figure 2: Hydrological and Geochemical Time series for LG (black, A) and KS (red, B).** Vertical
827   black shading in A shows outburst events recorded during the melt season (Kohler et al., 2017) and
828   vertical red shading in B shows the "Spring Event" at KS (Hawkings et al., 2016).

829   **Figure 3: Major ion ratio time series.** Ratio of Divalent/Monovalent ions (D:M) Differences in the
830   seasons (i.e. Late and Early Season) are defined by differences in hydrological and geochemical data
831   in the proglacial river.

Figure 4: Na-normalised molar ratio mixing diagrams. Silicate and carbonate endmembers taken from Gaillardet et al. (1999) and references within, using data from small rivers draining one single lithology.

Figure 5: Silicon isotope composition results. A) The relationship between $\delta^{30}DSi$ and D:M ion ratio. B) $\delta^{30}DSi$ and discharge for both catchments. C and D) Time series of $\delta^{30}DSi$ and $\delta^{30}ASi$ for KS and LG. Vertical blue shading in C indicates opening of the subglacial drainage system ("Spring Event", Hawkings et al. (2016)) and outburst events in D. Bulk bedrock $\delta^{30}Si$ is indicated by the horizontal dashed line, with the shading representing 2SD. All error bars represent 2SD of external errors (0.08 for $\delta^{30}DSi$ and 0.14 for $\delta^{30}ASi$).

Figure 6: Diagram to illustrate conceptual model of subglacial hydrology development. Simplified development of subglacial hydrology at LG as the melt season progresses. Panel A represents processes during the Early season of LG (before the first outburst event), B represents the system after the first outburst event and subglacial water influences the proglacial stream chemistry, and C represents the system during the late season once the snowline has retreated further and outburst events occur more often. The smaller size of KS limits the subglacial hydrology development to A and B, without the connection of isolated subglacial water by supraglacial lake drainage.

Figure 7: Major ion relationship plots. A) $Ca^{2+} + Mg^{2+}$ versus SO_4^{2-} B) $Ca^{2+} + Mg^{2+}$ versus HCO_3^- C) HCO_3^- versus SO_4^{2-}. Early Season at KS is defined as before the subglacial system connected (Day 157, Hawkings et al. (2016)), Transition Period is the hydrologically unique period after the subglacial connection and Late Season is post Day 169. Early season at LG is defined at prior to first outburst event/subglacial connectivity at day 170 and late season is defined as day 170 onwards. Grey dashed lines show main relationships found by Tranter et al. (2002) when studying an Alpine valley glacier. The table outlines the regression slopes, intercepts and R^2 values for each relationship.

Figure 8: Modelled Percentage ASi required for measured $\delta^{30}DSi$ composition. Panels A and B show the calculated f_a values according to Equation 7, with A (black) showing the time series at LG and B (red) showing the time series at KS. ε values represent the varying fractionation factors used in the model. Panels C (LG) and D (KS) show the concentration of ASi required to produce the measured DSi, compared to the measured ASi concentrations over the melt season.

Supplementary Figure 1: Estimated lake Residence Time at KS. Residence time of the proglacial lake at KS estimated by calculating the turnover rate of the lake using the estimated water volume of the lake and river discharge.

Supplementary Figure 2: Silicon three Isotope plot. All samples analysed during the study are included with red dashed lines showing the 95% prediction band and grey lines showing the 95% confidence band. The black regression line has a gradient of 0.5118 (p<0.0001, $R^2 = 0.9946$), showing mass dependent fractionation

Supplementary Figure 3: Relationship between $\delta^{30}DSi$ composition and saturation index of amorphous silica. Saturation indices calculated using Geochemists Workbench Software and plotted against $\delta^{30}DSi$ for both catchments. Data has been split into the defined hydrological periods of the melt season to show the temporal trend.

Supplementary Figure 4: Comparison of geochemical data with previously published data at LG. Records of discharge, D:M ratio and SO_4^{2-} from LG in 2009 (Hindshaw et al., 2014) and 2015 (this study).

Supplementary Figure 5: Sulphate Mass Fraction Timeseries. Calculated SMF for KS and LG over the melt season, with the seasons defined by hydrogeochemical data.

876 **Supplementary Figure 6: Relationship between SPM concentrations and dissolved silicon**
877 **isotope composition.**

Supplementary Tables

1 **Supplementary Table 1: Selected ionic concentrations from Leverett Glacier 2015, corresponding to timepoints in which silicon isotope measurements**
2 **were made**.

Decimal Day	Na$^+$ (μeq)	K$^+$ (μeq)	Mg^{2+} (μeq)	Ca^{2+} (μeq)	Al^{3+} (μeq)	SO4^{2-} (μeq)	NO3$^-$ (μeq)	HCO3$^-$ (μeq)	F$^-$ (μeq)	Cl$^-$ (μeq)
128.4	53.84	36.79	98.64	349.25	-	229.58	0.35	271.80	2.11	30.98
135.4	41.04	26.68	61.27	215.01	1.66	118.64	0.39	200.01	0.93	20.05
140.8	56.16	38.59	41.59	126.20	4.06	75.20	0.44	256.49	1.22	37.1
145.4	64.46	39.38	73.43	252.03	-	117.65	0.35	286.19	1.53	19.94
148.4	46.21	30.20	52.09	183.94	5.59	88.86	0.33	203.98	1.08	1487
153.4	88.11	48.69	52.26	262.81	2.03	161.33	0.15	260.72	3.14	24.90
160.4	67.06	38.06	42.93	220.05	12.62	122.06	0.31	222.43	1.90	18.24
165.4	49.13	25.40	24.07	123.15	2.50	59.27	0.08	145.82	1.18	14.58
171.4	55.46	28.05	20.89	102.54	1.56	47.75	0.18	143.14	1.07	12.95
174.7	44.83	16.96	13.71	58.35	1.98	24.71	0.16	87.43	1.31	18.68
178.4	65.73	29.85	19.74	87.76	20.78	45.21	0.08	148.22	1.43	7.25
183.4	66.15	37.57	20.31	83.19	22.94	37.66	0.16	159.93	1.54	6.24
186.4	50.78	24.61	14.56	65.33	-	26.79	0.19	119.10	0.92	6.34
189.4	47.50	20.29	13.47	60.33	139.81	23.70	0.15	111.80	0.94	3.48
191.4	48.82	22.10	15.99	75.44	15.09	31.13	0.18	124.23	0.98	4.05
196.3	36.56	16.10	13.40	65.53	16.01	25.13	0.13	99.53	0.85	4.59
200.4	44.98	20.55	12.40	73.24	61.02	38.46	0.09	105.85	0.98	4.83
207.4	52.17	23.93	13.88	89.36	58.96	45.75	0.10	128.46	1.46	2.53
208.4	59.20	26.68	14.14	106.63	69.25	54.22	0.10	146.83	1.35	3.09
210.3	53.30	24.34	16.37	95.11	78.68	47.20	0.12	136.60	1.38	2.64

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7 **Supplementary Table 2: Selected ionic concentrations from Kiattuut Sermiat 2013, corresponding to timepoints in which silicon isotope measurements**
8 **were made**.

Decimal Day	Na$^+$ (μeq)	K$^+$ (μeq)	Mg^{2+} (μeq)	Ca^{2+} (μeq)	Al^{3+} (μeq)	SO4^{2-} (μeq)	NO3$^-$ (μeq)	HCO3$^-$ (μeq)	F$^-$ (μeq)	Cl$^-$ (μeq)
111.59	47.92	29.14	63.53	442.50	5.10	66.13	0.07	477.37	19.01	24.51
124.48	45.32	28.32	53.57	404.70	-	70.94	0.23	417.08	18.15	22.96
139.50	45.22	29.46	54.62	378.04	-	75.97	0.23	387.05	17.65	23.91
149.50	46.24	29.47	56.42	397.38	-	82.29	0.32	398.28	18.39	26.13
150.50	42.33	27.46	51.81	373.51	6.64	82.68	0.32	363.79	19.03	25.91
155.52	42.37	27.34	49.55	358.36	7.24	73.93	0.30	359.86	16.12	24.21
159.50	36.44	24.16	42.55	296.01	-	59.01	0.26	303.08	12.14	21.92
162.63	30.68	21.43	36.56	264.80	-	50.45	0.26	268.78	11.86	19.41
170.90	24.47	18.84	28.39	224.87	17.44	29.96	0.19	251.22	9.11	12.73
172.68	22.96	18.03	27.04	224.71	19.92	26.37	0.16	244.61	8.57	11.29
178.50	21.14	17.23	26.89	227.25	-	22.92	0.15	250.96	7.44	9.39
181.50	19.95	16.37	25.15	226.12	-	22.27	0.12	246.50	8.09	9.24
194.52	18.88	14.46	25.91	218.87	-	20.43	0.09	240.61	8.43	7.47
205.54	15.01	11.96	21.04	179.89	-	14.43	0.08	200.92	6.53	4.99
207.50	13.18	10.44	17.51	147.3	-	13.76	0.09	161.89	6.71	4.99
212.53	14.65	11.22	19.34	181.91	13.53	15.05	0.06	198.67	7.41	5.26
220.63	13.56	10.52	17.92	167.17	11.73	15.04	0.05	180.46	7.82	5.17
221.6	13.14	11.01	16.93	164.53	-	14.15	0.03	191.17	6.68	4.57

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12   **Supplementary Table 3: Summary of Kiattuut Sermiat silicon isotope results from 2013.**

Decimal Day	Discharge (m^3s^{-3})	pH	Suspended Sediment $(g\ L^{-1})$	DSi (μM)	$\delta^{30}DSi$ (‰)	$\delta^{30}DSi$ error * $(2\sigma SD\ ‰)$	ASi (wt%)	$\delta^{30}ASi$ (‰)	$\delta^{30}ASi$ error * $(2\sigma SD\ ‰)$	Monovalent/ Divalent ions $(\mu eq\ L^{-1})$
111.6	0.7	8.29	0.04	40.59	1.01	0.05				6.57
124.5	2.6	7.79	0.04	39.29	0.79	0.18				6.22
139.5	3.6	8.08	0.11	36.60	0.71	0.08				5.79
149.5	7.0	7.94	0.25	38.45			0.24	-0.56	0.05	5.99
150.5	7.1	8.02	0.15	36.14	0.69	0.11				6.09
155.5	17.9	8.23	0.16	34.62	0.64	0.09				5.85
159.5	34.5	8.86	0.18	28.33			0.37	-0.54	0.05	5.59
162.6	27.6	8.85	0.13	26.76	0.47	0.10				5.78
170.9	34.4	9.19	0.13	22.70			0.05	-0.38	0.07	6.05
172.7	33.3	9.25	0.11	21.84	0.26	0.11				6.14
178.5	18.5	9.38	0.13	20.69			0.36	-0.42	0.06	6.62
181.5	19.5	9.38	0.12	20.90	0.25	0.11				6.92
194.5	43.3	9.46	0.10	20.68	0.38	0.08	0.16	-0.48	0.06	7.34
205.5	42.9	9.08	0.09	16.49	0.57	0.02				7.45
207.5	37.7	9.08	0.10	16.00			0.26	-0.42	0.06	6.98
212.5	36.2	9.13	0.10	16.49	0.41	0.09	0.24			7.78
220.6	29.9	9.48	0.08	16.79	0.16	0.14				7.67
221.6	29.9	9.34	0.09	15.92			0.18	-0.56	0.05	7.67

13   *Propagated internal error (2σ SD, ‰)

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18 **Supplementary Table 4: Summary of Leverett Glacier silicon isotope results from 2015**.

19

Decimal Day	Discharge $(m^3 s^{-3})$	pH	Suspended Sediment (g L^{-1})	DSi (µM)	δ^{30}DSi (‰)	δ^{30}DSi error * (2σSD ‰)	ASi (wt%)	δ^{30}ASi (‰)	δ^{30}ASi error * (2σSD ‰)	Monovalent/ Divalent ions (µeq L^{-1})
128.4	-	8.98	-	53.66	0.85	0.04	-	-	-	4.94
135.4	-	7.88	-	36.01	0.87	0.04	0.85	0.05	0.05	4.08
140.8	-	8.35	-	38.86	-		1.41	0.21	0.03	3.42
145.4	-	7.90	-	38.47	0.65	0.03	1.40	-0.16	0.03	3.13
148.4	5.4	7.72		35.63	-	-	-	-	-	3.09
153.4	13.0	7.85	0.54	37.00	0.66	0.04	1.03	-	-	2.30
160.4	17.5	7.80	0.53	31.51	0.60	0.02	0.75	-	-	2.34
165.4	25.1	7.64	0.56	24.13	0.37	0.03	0.86	-0.19	0.03	1.98
171.4	73.2	8.01	1.18	20.24	0.02	0.08	0.64	-	-	1.48
174.7	90.0	7.63	0.72	15.05	-0.23	0.02	-	-	-	1.17
178.4	122.7	8.41	1.37	24.85	-0.18	0.03	0.69	-0.20	0.04	1.12
183.4	215.1	9.18	2.09	27.69	-0.52	0.02	0.39	-0.15	0.03	1.00
186.4	207.2	8.33	0.85	19.75	-0.41	0.03	0.70	-	-	1.14
189.4	294.5	8.76	0.97	17.79	-0.41	0.03	0.83	-	-	1.09
191.4	360.9	9.24	1.05	21.41	-0.22	0.03	0.59	-0.27	0.04	1.29
196.3	230.1	8.58	0.66	16.29	-0.55	0.04	0.64	-	-	1.50
200.4	311.3	8.86	0.66	19.70	-0.14	0.03	0.85	-0.32	0.03	1.31
207.4	301.9	9.53	0.70	22.02	-	-	0.54	-0.16	0.04	1.36
208.4	270.5	9.62	0.78	24.83	-0.09	0.03	0.31	-	-	1.41
210.3	236.3	9.51	0.83	23.63	-0.06	0.03	0.97	-0.11	0.03	1.44

20 *Propagated internal error (2σ SD, ‰)

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23   **Supplementary Table 5: Summary of Measured and Calculated values for Mass Balance Calculations at LG.**

	Up to Day 210	After Day 210*	Total*
Q (L)	1.27×10^{12}	6.04×10^{11}	1.88×10^{12}
% of Q for melt period	67.8	32.2	100
DSi Flux (µMol)	2.65×10^{13}	1.26×10^{13}	3.90×10^{13}
ASi Flux (µMol)	2.65×10^{14}	1.25×10^{14}	3.90×10^{14}
Total Si Flux (µMol)	2.91×10^{14}	1.38×10^{14}	4.29×10^{14}
% of DSi Flux for melt period	9.1	9.1	9.1
% of ASi Flux for melt period	90.9	90.9	90.9
Qwt δ^{30}DSi (‰)	-0.25	+2.20	NA
Qwt δ^{30}ASi (‰)	-0.22	-0.22	NA
Total δ^{30}Si (‰)	-0.21	+0.44	0.00

35   ***** All calculated values, except for Q, based on the percentage of Q measured before and after Day 210.
36

37   **Supplementary Table 6: Details of ASi concentrations taken from selected proglacial debris in front of LG.**

Sample Number	Date of Collection	Location	ASi (%)
1	30/5/2015	N67 03.909 W050 09. 795	0.02
2	30/5/2015	N67 03.912 W050 09.789	>0.01
6	2/6/2105	N67 03.758 W050 12.093	0.01

38

Figure1

Figure legend:

Outwash Plains/Moraines

Meltwater River/Fjord

Lakes
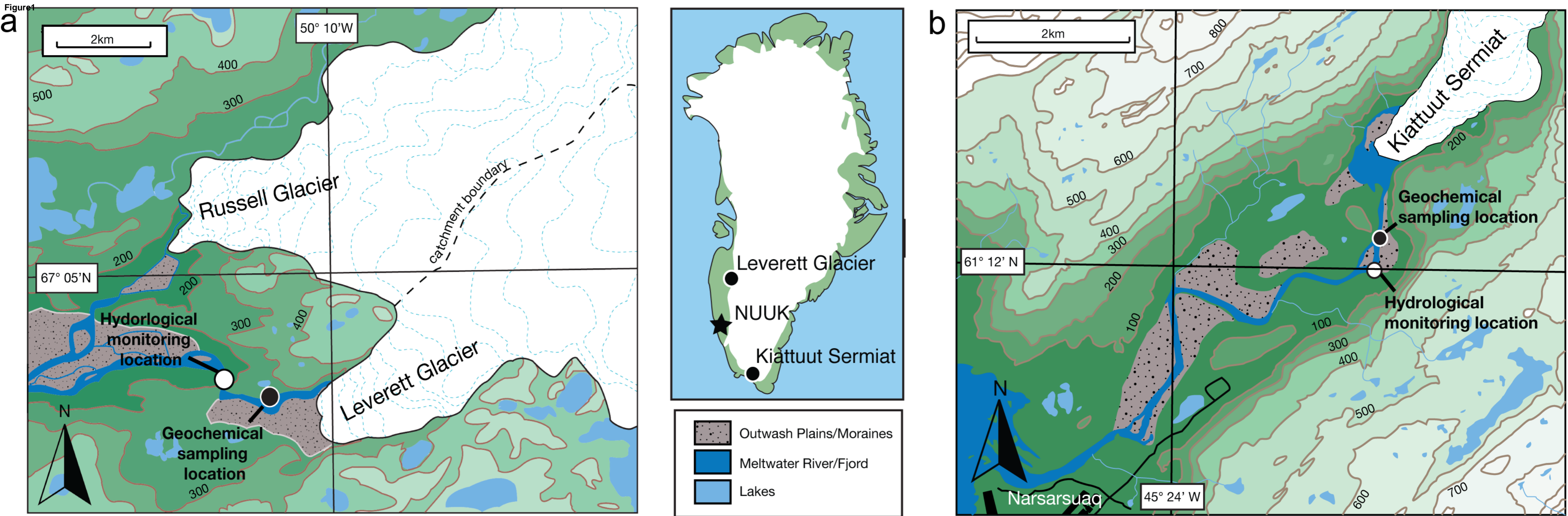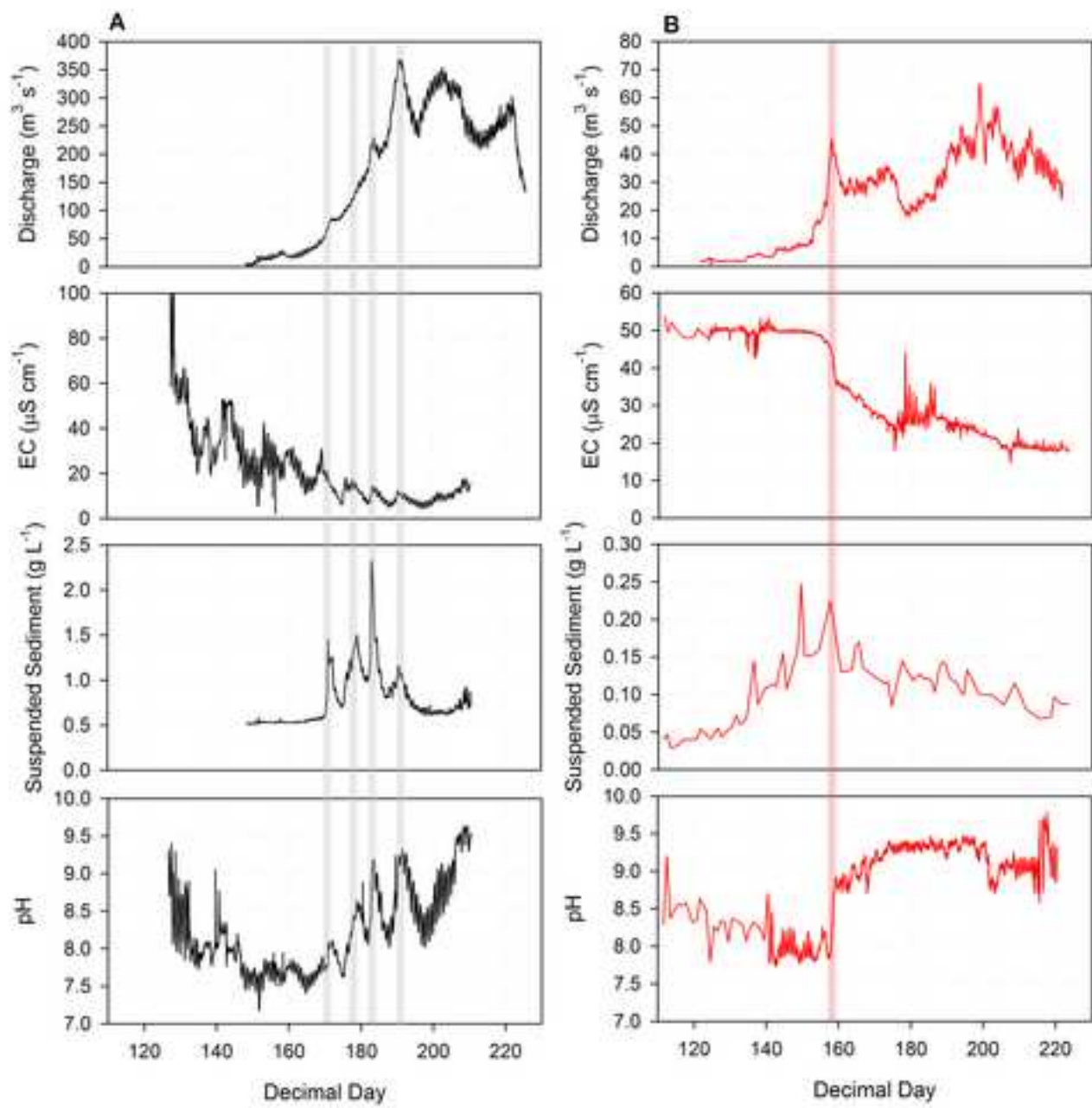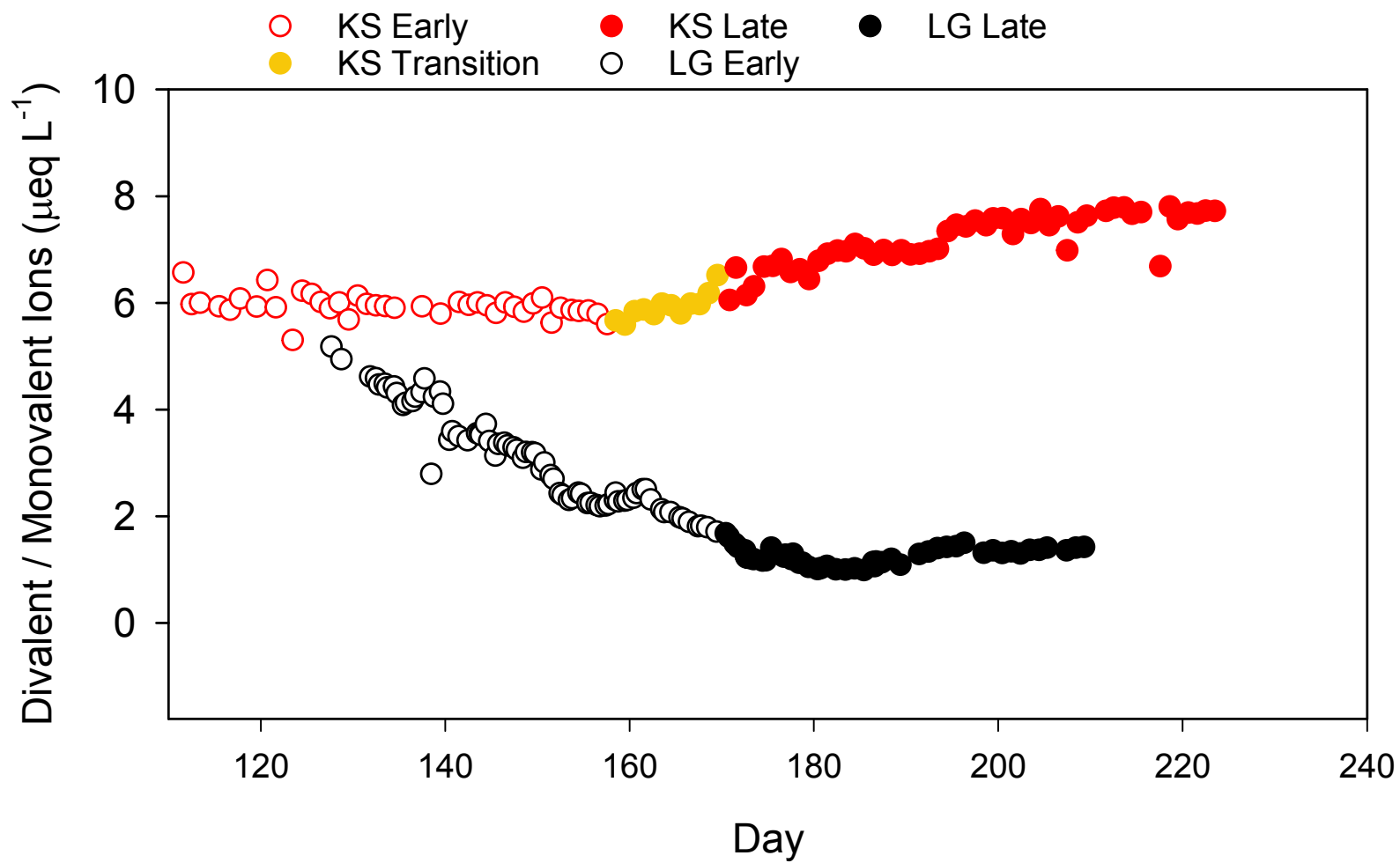
Figure2
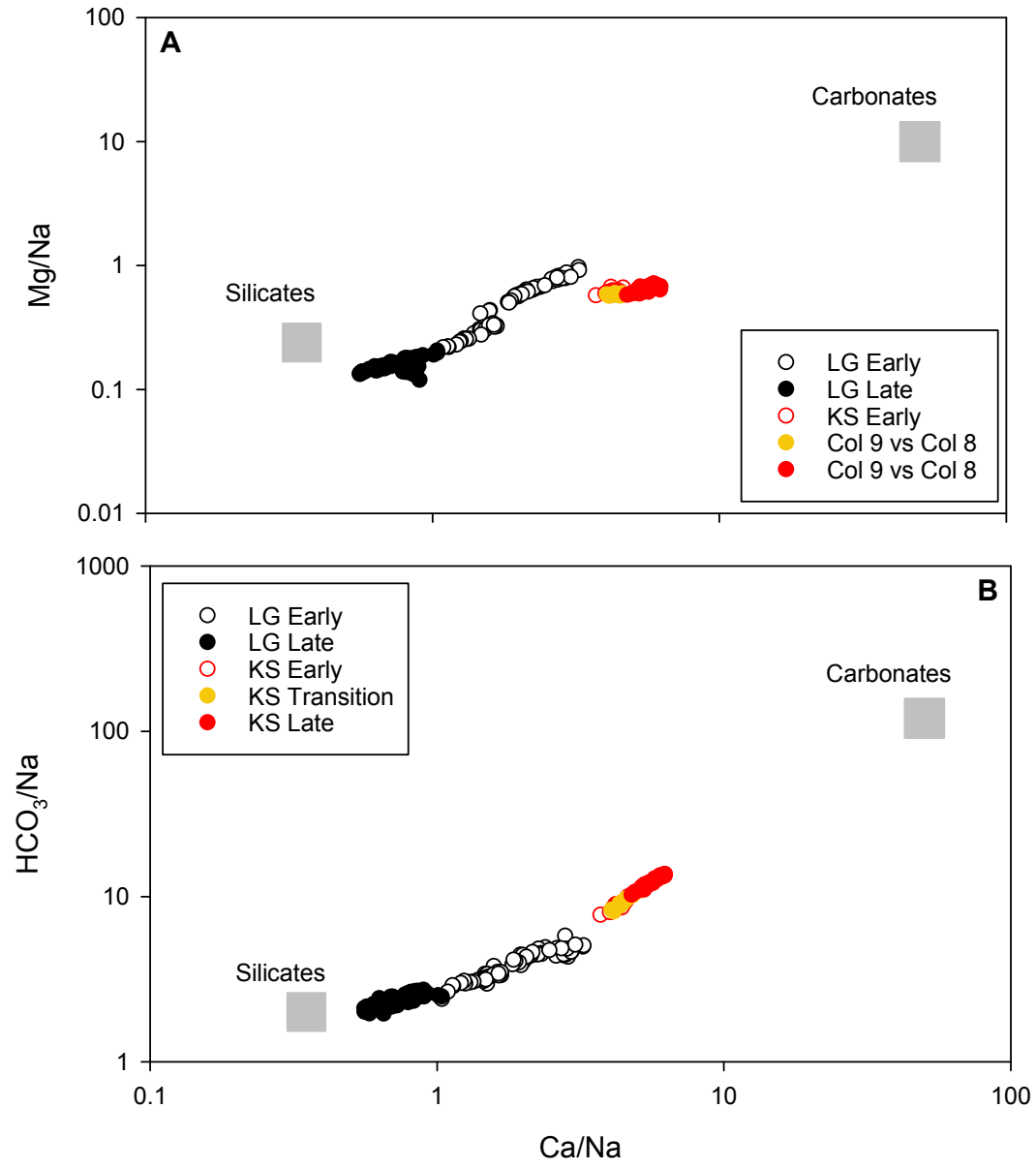
Figure3

Figure4

Figure5
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Figure6

Development of melt season

A Early Season

B Mid Season - Subglacial System Connected

C Late Season - Outburst Events

Bedrock

Snow covered

Ice

Isolated subglacial water

Crevasse

Proglacial Outlet

Direction of flow

Inefficient, distributed drainage

Supraglacial lake drainage

Snow covered

Bedrock

Ice

Isolated subglacial water

Direction of flow

Proglacial Outlet

Channelized drainage system, supraglacial lakes at the margin but still large isolated areas

Snow covered

Bedrock

Ice

Isolated subglacial water

Direction of flow

Proglacial Outlet

Channelized drainage system, supraglacial lake drainage and hydrological connectivity up to 40km inland

Figure7
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Figure8

SI Figure6

Equations