



1     **Combined diurnal variations of discharge and hydrochemistry of the Isunnguata Sermia outlet of the**  
2                                   **Greenland Ice Sheet give insight on subglacial conditions**

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5     **Abstract**

6             In order to examine daily cycles in meltwater routing and storage in the Isunnguata Sermia  
7     outlet of the Greenland Ice Sheet, variation in outlet stream discharge and in major element  
8     hydrochemistry were assessed over a six day period in July, 2013. Discharge was assessed from hourly  
9     photography of the outlet from multiple vantages, including where mid-stream naled ice provided a  
10    natural gauge. pH, electrical conductivity, suspended sediment, and alkalinity were measured in samples  
11    of stream water collected every three hours. Element and ion concentrations were subsequently  
12    measured in a laboratory setting.

13            Photography and stream observations reveal that although river width and stage have only  
14    slight diurnal variation, there are large changes in discharge shown in the portion of the width  
15    characterized by standing waves and fast flow. Width of this active channel approximately doubles over  
16    a diurnal cycle. Together with changes in flow over the naled, these features allow an observationally  
17    based relative record of stream discharge in this unconstrained alluvial setting. Peaks in discharge were  
18    offset by 3-7 hours from peak melt of the interior ice surface.

19            Concentration of dissolved solutes follows a sinusoidal diurnal cycle, except for large and  
20    variable increases in dissolved solutes during the stream's waning flow. Diurnal changes in solute  
21    concentration average 31% of the base value. Diurnal solute concentration minima and maxima lag peak  
22    and minimum stream discharge by 3-6 hours.

23            This phase shift between discharge and solute concentration suggests that during high flow,  
24    water is either encountering more rock material or is stored in longer contact with rock material. We



25 suggest that expansion of a distributed subglacial hydrologic network into seldom accessed regions  
26 during high flow could account for these phenomena, and for a spike of partial silicate reaction products  
27 during waning flow, which itself suggests a pressure threshold-triggered release of stored water.

28

## 29 **1. Introduction**

30 Dissolved load in glacial outlet streams has long been employed as a metric for assessing water-  
31 rock interactions occurring beneath glaciers and ice sheets. Glacierized basins have comparable  
32 dissolved loads to non-glacial rivers, but are enriched in mobile cations and depleted in Si (Anderson et  
33 al., 1997). Chemistry of glacial water suggests that observed solute concentrations are reached due to  
34 presence of reactive accessory minerals and fresh mineral surfaces in glacial sediments (Drever and  
35 Hurcomb, 1986). Dissolved load is therefore linked to physical erosion in subglacial environments  
36 (Anderson, 2005). Dissolved load is also indicative of the degree to which atmospheric gases have been  
37 sequestered by chemical processes in the subglacial environment (Hodson et al., 2000).

38 Diurnal variation of solute concentration is a potential indicator of meltwater routing and  
39 storage. Solute concentration is controlled by total water-rock contact during water residence time in  
40 the subglacial environment and by reactivity of minerals contacted by the water. In particular, two end  
41 member cases are expected: if dilution produces an inverse relationship between discharge and solute  
42 concentration, minimal changes in water-rock interaction over time are suggested, whereas if increased  
43 discharge is coupled to increased solute concentration, diurnal changes in processes of water-rock  
44 interaction or storage are suggested.

45 Studies of alpine glaciers have typically found solute concentration and discharge to vary  
46 inversely, with rising discharges corresponding to falling concentrations of dissolved solutes (Collins,  
47 1995; Hindshaw et al., 2011; Tranter et al., 1993). Ions produced by saturation limited reactions, such as  
48 calcite dissolution, can show increased load with discharge, but typically with diminished concentration



49 per water volume (Mitchell and Brown, 2007). Elements that are limited by factors such as the rate of  
50 sorption/desorption will have constant flux levels and will only be diluted by increased water flow  
51 (Mitchell and Brown, 2007). Resultantly, correlations between discharge and dissolved load are typically  
52 weak (Collins and MacDonald, 2004). These dilution relationships have been attributed to the  
53 dominance of conduit flow in alpine environments. In cases where subglacial water is confined to fixed  
54 conduits, increased water flow will expand the size of these conduits and the speed of through-flow but  
55 will have a minimal impact on the area of water-bed contact (Nye, 1976; Röthlisberger, 1972).

56 Studies of larger glacial systems suggest more complex water-rock interactions. In the outlet of a  
57 large glacierized basin in SE Alaska, increases in dissolved load lag spikes in discharge by several days  
58 (Anderson et al., 2003). Anderson and others attribute this to storage of water in a distributed system  
59 only released during the waning stages of flow. In distributed or linked-cavity flow, increased discharge  
60 allows flowing water to spread out across the glacier's bed and thereby increase the area of water-bed  
61 contact (Humphrey, 1987; Kamb, 1987). Time series data from the Watson River, near Kangerlussuaq,  
62 West Greenland, show out of phase variation in discharge and solute concentration, with maximum  
63 daily solute concentrations occurring as discharge is rising and minima occurring as discharge is falling  
64 (Yde et al., 2014). However, on the scale of the melt season as a whole, Yde and others find a strong  
65 inverse correlation between discharge and solute concentration, which they attribute to conduits  
66 carrying a substantially higher portion of the meltwater flow than the distributed subglacial system. Lags  
67 between minimum discharge and peak solute concentrations are also observed at Tsanfleuron Glacier,  
68 Swiss Alps (Zeng et al., 2012).

69 Seven measurements of dissolved solute chemistry taken from samples collected over the  
70 course of 2 days in 2011 at the terminus of a major west Greenland outlet glacier potentially show a  
71 direct relationship between solute concentration and discharge (Graly et al., 2014; Landowski, 2012). In  
72 this limited time series, solute concentration appears to peak at midafternoon, while discharge is high,



73 and be minimal in the early morning hours, with total variation of <20%. To further investigate whether  
74 a direct relationship between discharge and solute concentration exists in the Isunnguata Sermia outlet  
75 of the western Greenland Ice Sheet, we returned to the same site for a six day period of the summer of  
76 2013, collecting 8 samples per day for chemical analysis.

77

## 78 **2. Field site**

79 Water samples were collected from the terminus of Isunnguata Sermia, a major land-  
80 terminating outlet of the western Greenland Ice Sheet (Figure 1). The outlet glacier Isunnguata Sermia  
81 occupies a deeply cut glacial valley, with surrounding hilltops >400 m above sea level. Deep, glacially-  
82 carved trenches continue under the ice sheet for more than 20 km into interior, with ice depths of  
83 greater than 1,000 m (Jezek et al., 2013). The Isunnugata Sermia outlet has a catchment that  
84 encompasses >2,400 km<sup>2</sup> of the ablation zone, making it one of the largest regional subglacial drainage  
85 basins (Palmer et al., 2011). Regional geology consists of primarily of Paleoproterozoic gneisses and  
86 granitoids (van Gool et al., 2002). The Isunnguata Sermia outlet is located 25 km from the town of  
87 Kangerlussuaq. It is the next outlet to the north of the Russell Glacier and feeds a separate glacial river  
88 system from the Watson River.

89 Water emerges from a single location on the south side of Isunnguata Sermia's terminus front  
90 ~30m above sea-level (Figure 1) and traverses a broad, >100 km long sandur to the fjord. Discharge of  
91 pressurized subglacial water creates a large upwelling capable of expelling water multiple meters into  
92 the air and, although no fully quantitative measurement could be made, peak discharge was estimated  
93 to exceed 500 m<sup>3</sup>s<sup>-1</sup>. Ice-cored moraines and frozen outwash shape the course of outlet waters. On the  
94 sandur, frozen outwash channels the water into a single thread, although the large sediment load  
95 creates rapidly changing channel and bed geometry. Near the terminus, the frozen outwash of the  
96 sandur is elevated ~2-4 meters above the discharging stream. The main stream is also fed by minor ice



97 surface melt streams. A small stream that runs along the south lateral margin of the glacier joins the  
98 main terminal outlet stream just below the primary upwelling site.

99 This work was performed in the context of several other studies of the Isunnguata Sermia  
100 terminus. Hot water boreholes along a transect from the outlet to 40 km in the interior have provided  
101 data regarding water pressure (Meierbachtol et al., 2013), ice temperature (Harrington et al., 2015),  
102 subglacial water chemistry (Graly et al., 2014), and mass balance between subglacial sediment and rock  
103 (Graly et al., 2016). More limited datasets from Isunnguata Sermia's terminal and lateral outlets were  
104 reported for the 2010, 2011, and 2012 seasons (Graly et al., 2014). The work reported here is based on  
105 samples and data collected over a 6 day period from July 16<sup>th</sup> to July 21<sup>st</sup>, 2013.

106

### 107 **3. Methods**

#### 108 **3.1 Water Sampling**

109 Water sampling began at 8:00 hours local time on July 16<sup>th</sup>, 2013 and continued in 3 hour  
110 increments through 20:00 hours on July 21<sup>st</sup>, 2013. Samples were collected by lowering a liter bottle  
111 attached to a pole into discharging waters within 400 m of the subglacial upwelling. During July 16<sup>th</sup> and  
112 July 17<sup>th</sup>, samples were collected from the south bank of the outlet stream from the banks at the  
113 beginning of the outwash plain (Figure 1). During July 17<sup>th</sup>, the main course of the river shifted so that  
114 location had diminished flow and an emerging bank channeled waters from the lateral side stream to  
115 the location. Commencing at 14:00 hours on July 18<sup>th</sup>, sampling was relocated above the lateral side  
116 stream on the banks of the terminal moraine (Figure 1). The sampling location was not subsequently  
117 changed. Excepting periods where the emerging bank channeled lateral stream water to the first  
118 location, both locations sampled water from the main subglacial outlet and should produce comparable  
119 results.



120           Upon collection, 125 ml of water sample were pumped through 0.1  $\mu\text{m}$  nylon filters, with  
121 filtered water and filter papers saved for laboratory analyses. A colorimetric alkalinity test, a  
122 conductivity measurement, and a pH measurement were performed on the remaining unfiltered  
123 sample. Alkalinity tests were performed with a Hach Model AL-AP alkalinity test kit. Results of field  
124 alkalinity tests were only accurate to 25  $\mu\text{M}$ . Alkalinity was therefore also calculated by charge balance  
125 from the other measured ions. pH measurements and conductivity measurements were performed with  
126 Beckman-Coulter  $\Phi$ 460 multi-parameter meter. pH was measured using a low ionic strength probe.

127           Subsequent water analyses were performed in the University of Wyoming Aqueous  
128 Geochemistry Lab. Concentrations of Si, Ca, Mg, Na, and K were measured on a Perkin Elmer Elan 6000  
129 inductively coupled plasma quadrupole mass spectrometer (ICP-MS). Concentrations of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  
130 and  $\text{F}^-$  were measured on a Dionex ICS 500 ion chromatograph. The filter papers were dried and  
131 weighed to assess suspended load.

132

### 133 **3.2 Discharge**

134           Discharge measurements of the outlet were difficult. There is no exposed bedrock near the  
135 stream to act either as an elevation reference or to stabilize the river bed. Obtaining accurate cross  
136 profiles of the stream was prohibitively dangerous, with high flows, collapsing banks, and a considerable  
137 flux of mobile ice blocks. Attempts to install a stage pole were frustrated by considerable stage variation  
138 over time associated with cutting and filling of the river bed and banks. Once the stream opens out from  
139 its restriction by remnant glacier ice near the upwelling, stage is poorly correlated with discharge. The  
140 stream instead scours sediment during the rising limb and deposits it on the trailing limb of the daily  
141 hydrograph. It was decided to assess only relative discharge. This was aided by repeat photography from  
142 two fixed locations.



143           Hourly stream photography began at 10:00 hours on July 18<sup>th</sup> and continuing through 20:00  
144 hours on July 21<sup>st</sup>. From one vantage point, the central upwelling of subglacial water was photographed  
145 from the south, as it poured out from around the moraine. This vantage captured a ~1 meter high, mid-  
146 channel naled formed from freezing of outlet waters during winter months. The naled was variably  
147 covered or exposed as discharge varied and acted as a stream gauge in this respect. This portion of the  
148 stream is restricted by frozen sediment and stream height is controlled by discharge.

149           A second vantage, from a rise above the south bank, captured a ~200m long stretch of the  
150 outlet stream. In this portion of the stream, increased discharge caused scour and expansion of the  
151 stream's active channel. Photography allowed assessment of relative active channel width. Large waves  
152 and faster velocities are confined to this active channel, allowing fairly unambiguous, though qualitative,  
153 determination of which portions of an overhead photograph comprise the active channel. The distance  
154 between the upstream end of a persistent, mid-stream point bar and a distinct feature on the south  
155 shore was measured on each photograph (Figure 1). The length of the portion of this transect  
156 characterized by large waves and flow features was also measured, allowing for the calculation of the  
157 percentage of the stream width contained by the active channel. The second vantage also allowed  
158 assessment of flow state and Froude number from the presence of features such as standing waves.

159           During the first two days of the sampling period, stream surface velocity was measured by  
160 repeated timing the motion of floating ice and other stream surface features down a 100 m section of  
161 the stream. Measurements were taken during morning, afternoon, and evening stages to assess  
162 variation in velocity associated with high and low flow.

163

### 164 **3.3 Interior Surface Melt**

165           In order to compare variation in terminus discharge to melt in the surface interior, we are also  
166 including discharge measurements from an interior ice sheet surface stream. The stream was gauged



167 during the summer of 2012, so data are not directly comparable to the measurements collected in 2013.  
168 However inasmuch as interior melt is primarily controlled by insolation, the stream's variation likely  
169 represents a typical pattern for the timing and scaling of diurnal summer surface melt fluctuations.

170 The surface stream was located at 67.2°N and 49.8°E, ~25 km from the terminal outlet. Stream  
171 height was gauged with a calibrated pole drilled into ice. Surface velocity was measured by timing  
172 floating ice along a course of known distance. Cross-sectional area was directly measured in the region  
173 where the gauge was emplaced and calibrated to gauge height. Transect slope was measured by pole  
174 and automatic level. Six measurements of surface velocity used to calculate an average Manning  
175 coefficient from the measured slope and hydraulic radius of the stream. Discharge was then calculated  
176 from change in gage height. Stage height was measured every half hour or hour for a period from 11:30  
177 6/18/12 to 20:00 6/21/12. During June 18<sup>th</sup>, 19<sup>th</sup>, and 20<sup>th</sup>, sunny weather predominated; June 21<sup>st</sup> had  
178 rainy, cooler weather.

179

## 180 **4. Results**

### 181 **4.1 Discharge**

182 Over the four days during which repeat photographic observations were made, photographs of  
183 the naled show consistent minima at 8:00 hours, with the naled is mostly exposed, and a small volume  
184 of water overtopping a portion of the ice body (Figure 2). During the first two days of observation, the  
185 naled was completely covered by flowing water from 19:00 to 0:00 hours. On the third day it was  
186 covered from 16:00 hours, and remained covered for the remainder of the study period.

187 Maximum discharge is harder to determine from observations of the naled alone. Once the  
188 naled is completely covered in water, visual interpretation of maximum flow is ambiguous. Some  
189 discrimination can be made based on height of the covered naled feature compared to the surrounding  
190 waves and angle at which the water pours over the naled (greater flows overtop the naled at a lower





191 angle). From these features, maximum stream flow appears to occur at 21:00 hours on July 18<sup>th</sup> and  
192 19<sup>th</sup>, and 20:00 hours on July 20<sup>th</sup>.

193 Standing waves are observed at all flows (Figure 2), although substantial differences in wave and  
194 surface morphology were noted during waxing and waning phases, with rougher water in waning flow  
195 and smoother water in waxing flow. The roughness change may represent a change in the sediment load  
196 of the river between the erosive waxing stage and the depositional waning stage. The persistence of  
197 standing waves implies near critical flow conditions, or a Froude number approximately 1, for the entire  
198 study period. Measurements of stream velocity showed surface speeds of  $2.86 \pm 0.12$  m/s ( $2\sigma$ ,  $n=6$ ).  
199 Variation in velocity between morning and evening stages was within measurement error. Based on  
200 calculations from a Froude number of 1, stream depths of 0.5 - 0.9 m are suggested; these depth  
201 estimates were supported by observing ice blocks rolling or bouncing down the flow. The lack of  
202 relationship between stage and discharge and velocity has been noted before in sediment laden glacial  
203 rivers (Humphrey and Raymond, 1994).

204 Since neither stream velocity nor depth change with discharge, variations in discharge are  
205 accommodated by changes in the width of the active channel. Wide areas of shallow slow water  
206 remained present during low flows and the total surface area of the stream remained approximately  
207 constant. Pole probing of these shallow areas suggests 10 to 20 cm depths. Because the active channel  
208 has an order of magnitude greater discharge per transect meter than the marginal areas and changes in  
209 active channel water velocity were not observed, cross-sectional area of the active channel is the  
210 primary control on discharge.

211 Assessment of the active channel width shows substantial differences between morning hours  
212 (~5:00-10:00), where 20-30% of the stream is comprised of active channel characteristics, and late  
213 afternoon / evening hours (~18:00-0:00) where >40% of the stream is comprised of active channel



214 characteristics. These observations are generally consistent with assessments of the height of water  
215 pouring over the naled (Figure 3).

216

#### 217 **4.2 Interior Surface Stream**

218 The calculated Manning coefficient for the interior stream was  $0.0117 \pm 0.0018$  ( $2\sigma$ ). Discharge  
219 measured in the interior ice surface stream varied by as much as an order of magnitude during the  
220 course of diurnal cycles, with low values as small as  $0.3 \text{ m}^3\text{s}^{-1}$  and high values greater than  $3.5 \text{ m}^3\text{s}^{-1}$   
221 (Figure 3). Minimum stage heights consistently occurred around 4:00 hours. Maximum stage heights  
222 consistently occurred at 14:00 or 15:00 hours. These data contrast with our observations of water  
223 pouring over the naled. The naled minimum occurred approximately 4 hours later than minimum of  
224 surface melt. The naled maximum occurred approximately 6 hours later than maximum surface melt.  
225 This delay is representative of the integration of the travel time delays from the entire glacier  
226 catchment.

227

#### 228 **4.3 Water Analyses**

229 Sampled waters are generally chemically dilute, with  $292 \pm 50$  micromoles per liter dissolved  
230 solutes (Table 1). Ca is the dominant cation, followed by Na, K, and Mg (Figure 4). Mg abundances are an  
231 order of magnitude lower than the other major cations. Dissolved Si occurs at comparable abundance to  
232 Na. Standard deviations of the mass spectrometer measurements were  $<1\%$  of the measured value.  
233 Bicarbonate (measured as alkalinity) is the dominant anion.  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  are detected in all samples, but  
234 occur at an order of magnitude lower concentration. Trace amounts of  $\text{NO}_3^-$  and  $\text{F}^-$  were detected in  
235 some samples, at values an order of magnitude below  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  concentrations (Figure 4). On  
236 average, field alkalinity measurements exceed the alkalinity estimates from charge balance by  $25 \pm 14$   
237  $\mu\text{M}$  ( $2\sigma$ ). Some over-measurement in the field titration is expected, as the value is recorded at the level



238 where the color tracer disappears (and therefore is a maximum compared to previous drop). Charge  
239 imbalance may also result from absorption of  $H^+$  particles to suspended sediment in unfiltered water.  
240 Field electrical conductivity measurements show similar results to the laboratory analyses ( $p < 0.0001$ )  
241 (Figure 4). Suspended sediment concentration does not show a consistent correlation or anti-correlation  
242 with dissolved load (Figure 4).

243 Relative abundances of cation species is comparable to measurements taken at the Isunnguata  
244 Sermia terminus in the summer of 2011 (Graly et al., 2014). The  $SO_4^{2-}$ /alkalinity ratios are diminished  
245 compared to those measured in 2011, but are comparable to those found in samples collected in 2010  
246 and 2012. The concentrations of suspended sediment are similar to those observed at nearby Leverett  
247 Glacier during the summer of 2010 (Cowton et al., 2012).

248 When normalized to average concentration, magnitude and timing of cation and silica  
249 concentration variation is highly consistent between species over time (Figure 5). Covariation of all  
250 cation and Si species is statistically significant with  $p < 0.05$ . Covariations of K-Mg, K-Si, and Na-Si have  $p$ -  
251 values ranging from 0.01 to 0.05; all others are  $< 0.0001$ . All cations and silica concentrations follow a  
252 diurnal pattern with higher concentrations during morning and early afternoon hours and significantly  
253 lower concentrations during later afternoon and evening hours. In several of the studied cycles, large  
254 changes in total concentration are limited to the 20:00 and 23:00 hours samples, which are substantially  
255 lower than the other samples collected throughout the day.

256 There are two major deviations from the diurnal pattern. The 11:00, 14:00, 17:00, and 20:00  
257 samples from July 17<sup>th</sup> have substantially lower concentrations than would be otherwise suggested by  
258 diurnal fluctuations observed elsewhere in the record. This corresponds with the period during which an  
259 emerging bank partially separated site 1 from the main channel allowing a surface-fed side stream to  
260 substantially dilute the water.



261 At 2:00 on July 20<sup>th</sup>, there is a >60% spike in total concentration of all cations. Similar, but  
262 smaller magnitude spikes are also present in the 2:00 samples of July 19<sup>th</sup> and 21<sup>st</sup> and the July 16<sup>th</sup>  
263 23:00 sample. The most clearly expressed of these spikes (July 20<sup>th</sup> and 21<sup>st</sup>) are substantially more  
264 expressed in Na and K concentrations than in Ca, Mg, or Si. During the July 21<sup>st</sup> spike, the spike in Mg  
265 and Si appears to precede the spike in Ca, Na and K in that it appears during the previous sampling  
266 period. Large variability in the magnitude of these spikes suggests that the 3-hour sampling schedule  
267 was insufficiently frequent to characterize them entirely.

268 Anions generally follow similar patterns, but with greater variability (Figure 4). In particular, Cl  
269 does not co-vary with other ions toward the end of the record. The spike on July 18<sup>th</sup> coincides with a  
270 drop in SO<sub>4</sub> concentration; the spike on the 20<sup>th</sup> coincides with a drop in Cl concentration. SO<sub>4</sub>  
271 concentrations generally only minimally increase during the spikes.

272 Excluding these anomalies, the highest concentration of dissolved solids occurs at 11:00 on July  
273 16<sup>th</sup>, 19<sup>th</sup>, 20<sup>th</sup>, and 21<sup>st</sup> (Figure 5). On July 17<sup>th</sup> and 18<sup>th</sup>, the 11:00 sample was likely diluted by the side  
274 stream (which was a significant component of flow to site 1 during that period). Concentration minima  
275 are reached at 23:00 hours on July 17<sup>th</sup> through 20<sup>th</sup>. On July 16<sup>th</sup>, the minima occurs in the 20:00  
276 sample. The size of the diurnal variation varies from 22% to 49% of the lowest value, with an average  
277 daily range of  $31 \pm 9\%$ .

278

## 279 5. Discussion

### 280 5.1 Discharge and Outlet Stream Observations

281 Observations from oblique photography suggest large diurnal changes in discharge. Width of the  
282 active channel, with deeper faster water, approximately doubles in the course of the day (Figure 3b). An  
283 approximate doubling of discharge is also suggested by observations of the midstream naled. The naled  
284 is of comparable scale to the depth of the stream (both order of 1 meter). Its exposure during low flow



285 and burial during high flow suggests a change in stage comparable to its height. At the naled site,  
286 increased width of active channel flow is restricted by ice. Increases in flow height at the naled location  
287 are therefore approximately equivalent to increases in active channel width downstream.

288 During high flows, diurnal increases in discharge of up to 50% of base value are observed in the  
289 Watson River at Kangerlussuaq, where a bridge over a narrow gorge has allowed for the construction of  
290 a reliable gauge (Hasholt et al., 2013). As the Watson River is 20-30 km from its glacial outlet sources  
291 and integrates several independent glacial outlet streams, these diurnal cycles are likely muted  
292 compared to their expression at the ice margin. Larger diurnal changes are therefore expected directly  
293 at glacier outlet termini. Contrastingly, Smith and others (2015) found minimal diurnal variation in  
294 discharge at Isunnguata Sermia terminus. However, as Smith and others estimated discharge based  
295 solely on the surface area of the outlet stream water, their analysis missed the variation in the width of  
296 the active channel and height of its flow over static features that we present.

297

## 298 *5.2 Diurnal Changes in Solute Flux*

299 The critical observation is that variability in the dissolved solute concentrations cannot be  
300 explained by dilution alone. First, the scale of discharge variation is substantially larger than variation in  
301 concentration of dissolved solutes. Approximate width of the main channel doubles during diurnal  
302 cycles, while concentrations of dissolved solutes only change by an average of 21-40% (Figure 5).  
303 Secondly, maximum and minimum solute concentrations are offset from minimum and maximum  
304 discharge. Such lags imply periods where solute concentration is increasing even as discharge rises and  
305 periods where solute concentration is falling even as discharge falls.

306 Periods of in-phase changes between discharge and solute concentration suggest that increased  
307 water flow is either stimulating increased water-rock interaction or allowing for release of stored water  
308 (that has developed higher solute concentrations over longer residence times). While the single



309 upwelling structure of the terminus of Isunnguata Sermia implies local channelized flow, observations of  
310 water pressures at interior sites (Meierbachtol et al., 2013) and hydrologic theory for low ice surface  
311 slopes (Werder et al., 2013) both suggest that much of the catchment interior has a linked-cavity flow  
312 system. Linked cavity systems would allow for expansion of the basal hydrological system and flushing of  
313 long water residence time regions under high flow conditions.

314 Sudden increases in solute concentration during waning flow suggest that discharge from  
315 subglacial regions with a high concentration of dissolved solutes is triggered when a threshold is  
316 reached. Multiple triggering mechanisms are plausible. Modeling of subglacial water pressures suggests  
317 that near the ice sheet margin, water flows from conduits to the distributed cavity system at high  
318 conduit water pressures and back to conduits at low pressures (Meierbachtol et al., 2013). Solute  
319 concentration spikes result from the crossing of a pressure threshold allowing water stored during high  
320 flow to suddenly enter the glacial outlet system.

321 Solute concentration spikes might also be explained by creep closure of linked cavities that  
322 opened during high flow and expulsion of remaining solute-concentrated water. Anderson and others  
323 (2003) proposed a similar creep closure mechanism to explain increases in solute concentration during  
324 waning flow that occurred on a multiday scale in a mountain glacier setting. Following the Glenn-Nye  
325 relation, the rate of creep closure of ice scales to approximately the third power of effective pressure  
326 (Cuffey and Paterson, 2010). Differences in timing of these effects between ice sheets and mountain  
327 glaciers can therefore be explained by differences in ice thickness.

328 Relative dominance of Na and K in these spikes is consistent with water-rock interactions  
329 occurring only over a limited time, such that cation exchange occurred on fresh feldspar and mica  
330 surfaces but complete silicate dissolution and clay precipitation did not (Blum and Stillings, 1995; Graly  
331 et al., 2014). Contrastingly, constituents associated with weathering of reactive accessory minerals such  
332 as pyrite and calcite (especially  $\text{SO}_4$ ) are minimally expressed. This implies that the spikes' composition



333 reflects waters that have rapidly passed through reactive sediment that is depleted of accessory  
334 minerals. Such accessory mineral depletion can occur if sediment residence time in the subglacial  
335 system is sufficiently long (Graly et al., 2014). Sampling of sediment beneath ice boreholes has shown  
336 the greatest chemical depletion in portions of the ice sheet most likely to be influenced by distributed  
337 flow (Graly et al., 2016). This suggests that the spike of chemical solutes comes from water that has  
338 temporarily entered regions of distributed flow as a part of a diurnal cycle.

339

#### 340 **6. Conclusions**

341 A semi-quantitative discharge record can be constructed through hourly photographic  
342 monitoring of the static and dynamic features of a large, sediment laden glacial outlet stream. These  
343 assessments show large diurnal changes in discharge over the six day study period at the Isunnguata  
344 Sermia outlet of the Greenland Ice Sheet (c.f. Smith et al., 2015). Simultaneously collected chemical  
345 measurements show substantially smaller fluctuation in dissolved load; thus this Greenland outlet  
346 glacier does not show the discharge-driven dilution of solute concentration that is common in smaller  
347 ice masses. Periods where dissolved solute concentration increase and decrease along with discharge,  
348 and abrupt and variable increases in solute concentration during waning flow imply that significant  
349 contributions to the solute load is made by changes to the routing and storage of meltwater in the  
350 subglacial system over the course of the day. In particular, these results indicate considerable exchange  
351 of water diurnally between the conduit and linked cavity drainage systems, as well as implying threshold  
352 pressure conditions for these exchanges.

353

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357

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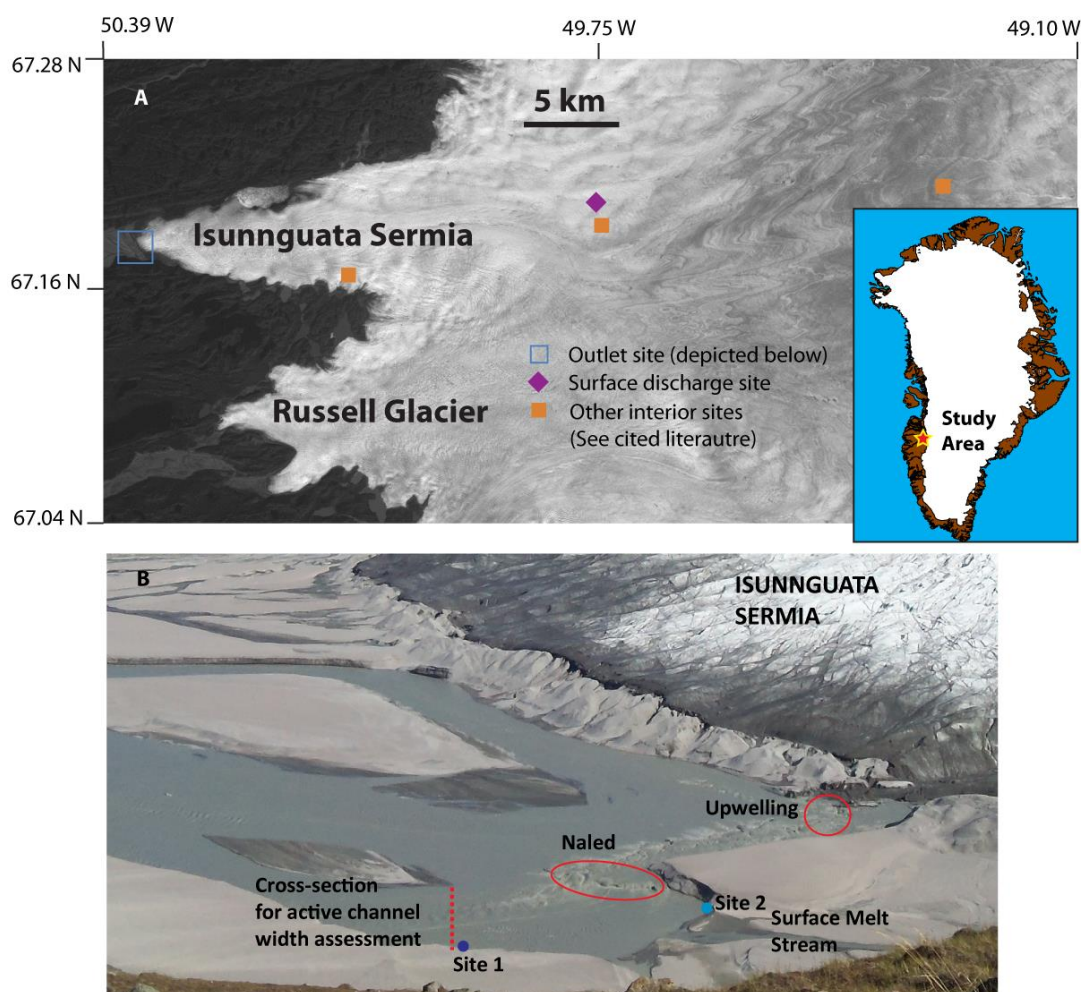
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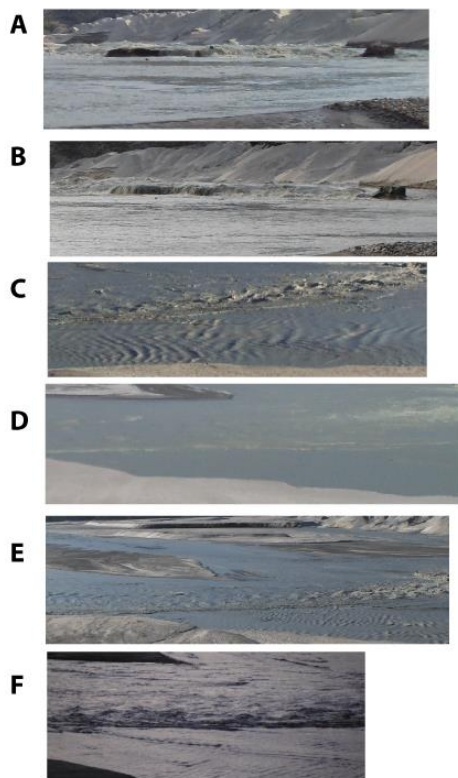
433 **Figures:**



434

435 **Figure 1.** A) Location of the study area. B) Overhead photograph of the study area (taken 7/22/13) with  
436 important sampling and observational features. Samples were collected at site 1 from 10:00 hrs on  
437 7/16/13 through 11:00 hours on 7/18/13. Samples were collected at site 2 from 14:00 hrs on 7/18/13  
438 through 20:00 hrs on 7/22/13. Beginning at 10:00 hrs on 7/18/13, hourly photographs on the labeled  
439 naled and ~100 m cross-section were taken.

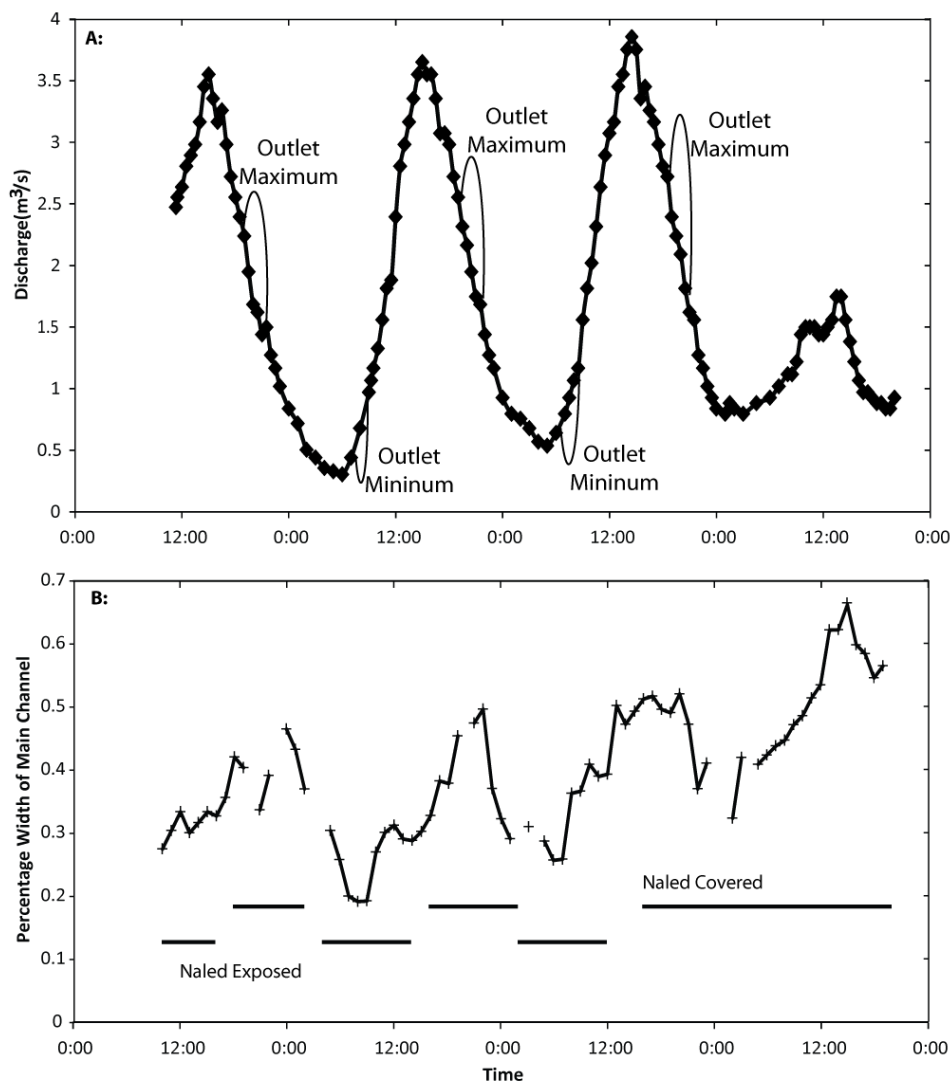
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442 **Figure 2.** Photographs of typical flow patterns in the Isunnguata Sermia outlet. A) Midstream naled  
443 exposed at during low flow (8:00). B) Midstream naled covered during high flow (21:00). C-F show flow  
444 during low (8:00), waxing (14:00), high (21:00) and waning (0:00) stages. Waxing and waning stages  
445 show different wave morphology but maintain standing wave features.

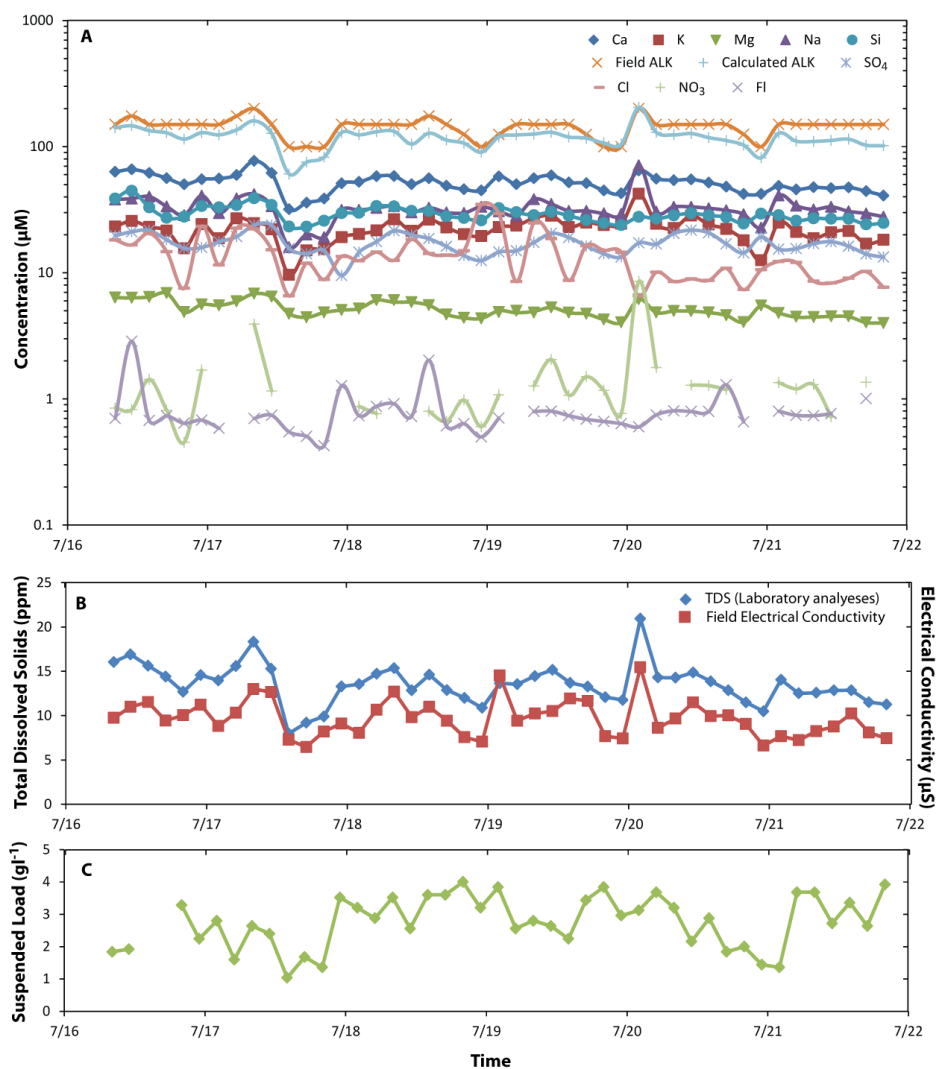
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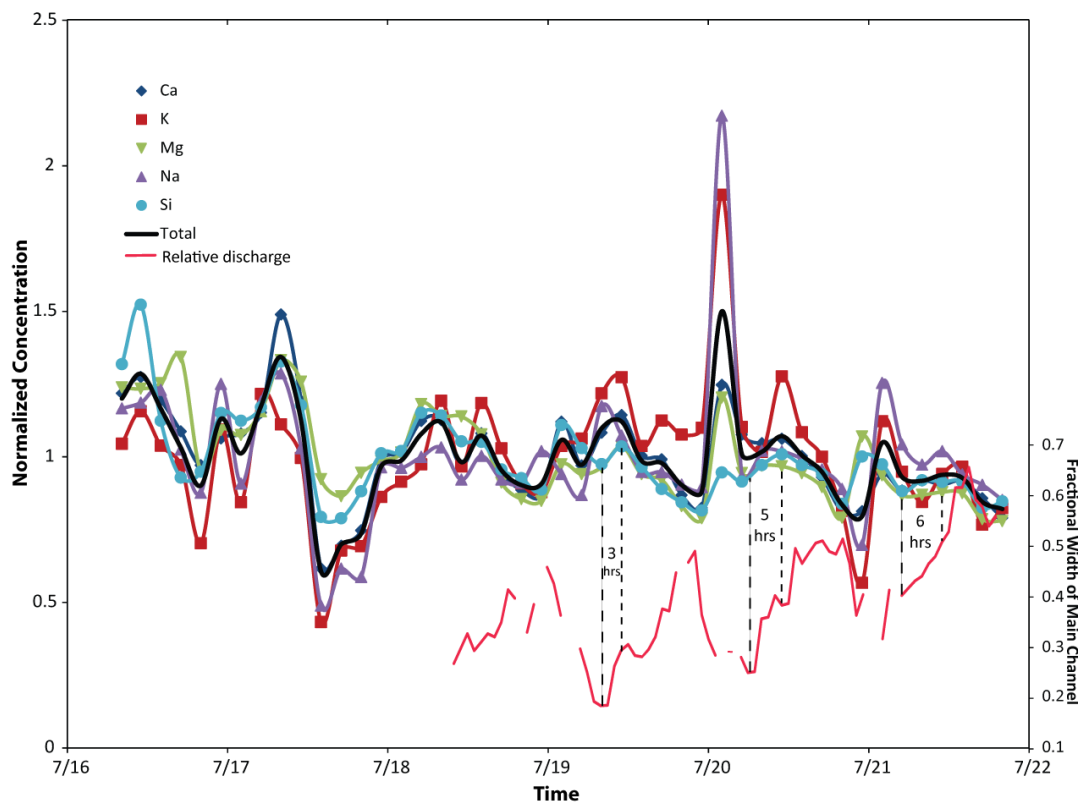
448 **Figure 3.** A) Measured discharge in an interior surface stream over a 4 day period in 2012 compared to  
449 time ranges of maximum and minimum discharge as suggested by flow volumes over midstream naled  
450 ice in the outlet of Isunnguata Sermia during the study period. B) Assessment of percentage of distance  
451 between a point bar and the shore that is characterized by large waves suggestive of deep, fast flow.  
452 Periods of time where the midstream naled is exposed and covered are included for comparison.

453



454

455 **Figure 4.** A) Concentration of dissolved constituents in sampled waters over time, including laboratory  
456 measurements of cations and Si by ICP-MS, anions by ion chromatography, and field measurements of  
457 alkalinity (ALK). Alkalinity as calculated by charge balance is also depicted. B) Total dissolved solids from  
458 the sum of the laboratory measurements and charge balance alkalinity (HCO<sub>3</sub>) compared to field  
459 conductivity measurements. Co-variation is statistically significant ( $p < 0.0001$ ). C) Dry weight of  
460 suspended sediment on filters.



461

462 **Figure 5.** Concentration of dissolved cations and Si normalized to average concentration. Discharge from  
463 relative active channel width is shown for comparison. Lags between active channel width channel  
464 minima and solute concentration maxima are illustrated with dashed lines.

465





466 **Tables:**

467

468 **Table 1. Field and laboratory measurements (results in micro-molarity unless otherwise noted)**

Sample	Time	pH	Electrical Conductivity (µS)	Suspended Sediment (g l <sup>-1</sup> )	Field Alkalinity (µM)	Ca	K	Mg	Na	Si	Fl	Cl	NO <sub>3</sub>	SO <sub>4</sub>	Calculated Alkalinity
GL13-1	7/16/2013 8:10	8.59	9.74	1.84	150	63.11	23.24	6.36	38.12	38.67	0.70	18.24	0.85	19.67	141.17
GL13-2	7/16/2013 11:00	8.82	10.98	1.92	175	65.99	25.72	6.33	38.77	44.68	2.86	16.65	0.82	21.16	146.46
GL13-3	7/16/2013 14:00	8.70	11.54	NA	150	61.88	23.10	6.43	40.20	32.96	0.67	20.58	1.43	21.68	133.87
GL13-4	7/16/2013 17:00	8.70	9.44	NA	150	56.32	21.61	6.89	33.53	27.25	0.73	14.71	0.81	18.27	128.76
GL13-5	7/16/2013 20:00	8.65	10.04	3.28	150	50.31	15.65	4.87	28.65	27.84	0.64	7.53	0.45	15.63	114.79
GL13-6	7/16/2013 23:00	8.75	11.22	2.24	150	55.07	24.32	5.60	40.89	33.75	0.68	23.38	1.69	15.88	129.06
GL13-7	7/17/2013 2:00	8.73	8.82	2.80	150	55.96	18.77	5.52	29.67	32.96	0.58	11.53	<0.45	17.62	124.03
GL13-8	7/17/2013 5:00	8.84	10.32	1.60	175	59.65	27.05	5.94	38.90	34.34	<0.43	22.57	<0.45	19.35	135.86
GL13-9	7/17/2013 8:00	8.90	13	2.64	200	77.11	24.73	6.83	42.06	38.95	0.70	22.27	3.91	23.84	160.13
GL13-10	7/17/2013 11:00	8.51	12.66	2.40	150	61.76	22.14	6.46	33.64	34.54	0.74	15.23	1.16	23.85	127.40
GL13-11	7/17/2013 14:00	8.01	7.28	1.04	100	31.93	9.62	4.74	15.96	23.29	0.55	6.56	<0.45	15.56	60.69
GL13-12	7/17/2013 17:00	8.32	6.46	1.68	100	35.97	15.07	4.44	20.12	23.15	0.51	11.90	<0.45	14.14	75.32
GL13-14	7/17/2013 20:00	8.62	8.2	1.36	100	38.71	15.41	4.85	19.19	25.86	0.43	8.85	<0.45	14.99	82.45
GL13-15	7/17/2013 23:00	8.80	9.1	3.52	150	51.23	19.17	5.06	31.51	29.70	1.27	13.49	<0.45	9.54	129.42
GL13-16	7/18/2013 2:00	8.71	8.04	3.20	150	52.52	20.33	5.21	31.44	29.94	0.74	12.48	0.87	14.55	124.02
GL13-17	7/18/2013 5:00	8.53	10.66	2.88	150	58.17	21.66	6.06	32.69	33.77	0.87	14.59	0.76	17.66	131.26
GL13-18	7/18/2013 8:00	8.90	12.7	3.52	150	58.34	26.52	5.85	33.74	33.52	0.92	12.56	<0.45	21.50	132.18
GL13-19	7/18/2013 11:00	8.48	9.82	2.56	150	50.27	21.52	5.84	30.12	30.90	0.73	18.38	<0.45	19.98	104.80
GL13-20	7/18/2013 14:00	8.53	10.98	3.60	175	56.00	26.34	5.53	32.80	30.84	2.03	14.21	0.80	18.63	127.88
GL13-21	7/18/2013 17:00	8.66	9.42	3.60	150	48.92	22.88	4.68	30.15	28.08	0.61	13.82	0.66	16.16	112.80
GL13-22	7/18/2013 20:00	8.61	7.56	4.00	125	45.92	20.21	4.39	29.79	27.19	0.64	14.99	0.98	13.68	106.64
GL13-23	7/18/2013 23:00	8.60	7.06	3.20	100	44.93	19.53	4.35	33.33	26.04	0.50	34.89	0.60	12.51	90.43
GL13-24	7/19/2013 2:00	8.68	14.54	3.84	125	58.06	23.07	5.00	30.77	32.56	0.71	29.45	1.08	14.63	119.46
GL13-25	7/19/2013 5:00	8.27	9.42	2.56	150	50.26	23.64	4.83	28.40	30.22	<0.43	8.51	<0.45	14.96	123.76
GL13-26	7/19/2013 8:00	8.58	10.24	2.80	150	56.08	27.09	4.95	38.39	28.60	0.79	24.85	1.27	17.39	125.83
GL13-27	7/19/2013 11:00	8.70	10.5	2.64	150	59.22	28.32	5.32	35.07	30.39	0.80	18.63	2.05	20.54	129.90
GL13-28	7/19/2013 14:00	8.46	11.92	2.24	150	52.04	23.07	4.82	30.99	28.33	0.74	8.69	1.07	19.07	119.13
GL13-29	7/19/2013 17:00	8.35	11.66	3.44	125	51.33	25.01	4.73	30.98	26.10	0.69	16.41	1.50	16.31	116.88
GL13-30	7/19/2013 20:00	8.58	7.68	3.84	100	44.99	23.94	4.26	29.57	24.76	0.66	15.06	1.17	14.15	106.81
GL13-31	7/19/2013 23:00	8.58	7.42	2.96	100	42.73	24.46	4.05	29.26	23.92	0.64	14.57	0.77	13.32	104.67
GL13-32	7/20/2013 2:00	8.53	15.46	3.12	200	64.60	42.27	6.17	70.99	27.76	0.60	6.56	8.54	17.23	204.64
GL13-33	7/20/2013 5:00	8.03	8.62	3.68	150	55.74	24.52	4.85	30.50	26.84	0.75	10.08	1.78	16.88	129.83
GL13-34	7/20/2013 8:00	8.37	9.66	3.20	150	54.24	22.61	4.97	33.37	28.51	0.81	8.52	<0.45	20.50	124.06
GL13-35	7/20/2013 11:00	8.30	11.48	2.16	150	54.99	28.39	4.97	33.30	29.61	0.79	8.94	1.29	21.77	127.04
GL13-36	7/20/2013 14:00	8.39	9.94	2.88	150	51.93	24.12	4.84	32.49	28.51	0.79	8.71	1.28	20.74	117.89
GL13-37	7/20/2013 17:00	8.48	10.02	1.84	150	48.16	22.25	4.60	31.28	27.60	1.29	10.85	1.19	16.96	111.80
GL13-38	7/20/2013 20:00	8.69	9.06	2.00	125	42.10	18.12	4.06	29.09	24.59	0.66	7.35	<0.45	14.37	102.76
GL13-39	7/20/2013 23:00	8.12	6.62	1.44	100	42.13	12.60	5.49	22.80	29.38	<0.43	10.54	<0.45	19.25	81.60
GL13-40	7/21/2013 2:00	8.80	7.68	1.36	150	48.73	24.96	4.80	40.99	28.59	0.80	12.31	1.35	15.40	127.78
GL13-41	7/21/2013 5:00	8.20	7.22	3.68	150	45.80	21.11	4.45	34.07	25.88	0.74	12.08	1.20	15.56	110.55
GL13-42	7/21/2013 8:00	8.70	8.24	3.68	150	47.55	18.79	4.46	31.80	26.99	0.74	8.58	1.30	17.01	109.97
GL13-43	7/21/2013 11:00	8.42	8.76	2.72	150	46.89	20.93	4.51	33.33	26.81	0.76	8.28	0.72	17.63	112.03
GL13-44	7/21/2013 14:00	8.12	10.24	3.36	150	47.52	21.48	4.49	30.72	26.82	<0.43	9.04	<0.45	16.26	114.65
GL13-45	7/21/2013 17:00	8.32	8.08	2.64	150	44.42	17.05	4.03	29.55	24.22	1.01	10.22	1.36	14.10	102.73
GL13-46	7/21/2013 20:00	8.62	7.44	3.92	150	40.93	18.31	4.00	27.84	24.85	<0.43	7.66	<0.45	13.31	101.73

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