Chemical denudation and the role of sulfide oxidation at Werenskioldbreen, Svalbard

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18 Abstract

19 This study aims to determine the rate of chemical denudation and the relationships between
20 dominant geochemical reactions operating in the proglacial and subglacial environments of
21 the polythermal glacier Werenskioldbreen (SW Svalbard) during an entire ablation season.
22 Water sampling for major ion chemistry was performed at a proglacial hydrometric station
23 and from subglacial outflows from May to September 2011. These data were combined with
24 measurements of discharge and supraglacial ablation rates. The slopes and intercepts in best-
25 fit regressions of [$\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. SO_4^{2-}] and [HCO_3^- vs. SO_4^{2-}] in meltwater from ice-
26 marginal subglacial channels were close to the stoichiometric parameters of sulfide oxidation
27 and simple hydrolysis coupled to carbonate dissolution (*concentrations corrected for input of
28 sea-salt). This shows that these relationships predominates the meltwater chemistry. Our
29 findings also show that sulfide oxidation is a better indicator of the configuration of subglacial
30 drainage systems than, for instance, Na^+ and K^+ . In the proglacial area and in sub-artesian
31 outflows, the ion associations represent sulfide oxidation but other processes such as ion
32 exchange and dissolution of Ca and Mg efflorescent salts may also contribute to the solute
33 variations. These processes may cause enhanced fluxes of Ca^{2+} and HCO_3^- from glacierised
34 basins during the early ablation and peak flow seasons as the proglacial salts re-dissolve. The
35 overall chemical denudation rate in the basin for 2011 (ranging from 1601 and 1762 meq m^{-2}
36 yr^{-1} (121.9 and 132.2 $\text{t km}^{-2} \text{yr}^{-1}$)) was very high when compared to other Svalbard valley
37 glaciers suggesting that the high rate of chemical denudation was mostly caused by the high
38 rates of discharge and ablation. Chemical weathering intensities (876 and 964 $\text{meq m}^{-3} \text{yr}^{-1}$)
39 exceeded previously reported intensities in Svalbard.

40 *Keywords:* Werenskioldbreen; sulfide oxidation; simple hydrolysis; carbonation; runoff;
41 Spitsbergen.

42

43 1. Introduction

44

45 Glacierised basins affect regional elemental cycles through weathering processes operating in
46 subglacial and proglacial environments (Gíslason et al., 1996; Hodson et al., 2000; Hawkings
47 et al., 2014; Yde et al., 2014). However, there is a general lack of knowledge of the coupling
48 between geochemical reactions in subglacial and proglacial environments and how these
49 reactions change throughout the ablation season.

50 Reactions that donate H^+ from the dissociation of organic and inorganic acids are
51 particularly crucial for chemical weathering processes in these and other systems (e.g. Appelo
52 and Postma, 2005), and in glacierised basins, H^+ ions are primarily derived from the
53 dissociation of inorganic acids such as sulfuric, carbonic or nitric acids (Tranter et al., 1993)
54 or simple hydrolysis (dissociation of H^+ from water, Tranter et al., 2002; Yde et al., 2005).
55 While simple hydrolysis only dominates during the early phase of contact between water and
56 minerals (Tranter and Wadham, 2013), sulfide oxidation and carbonation dominate in later
57 phases and are the two main acid forming reactions which often are responsible for chemical
58 weathering in glacierised catchments (Brown, 2002; Tranter et al., 2002). Sulfide oxidation in
59 particular, which is usually coupled to the dissolution of carbonates and silicates, is
60 potentially important in supporting primary productivity in oceans due to the delivery of iron
61 (oxyhydr)oxide to ocean waters (Raiswell et al., 2006; Hawkings et al., 2014). Based on ^{34}S -
62 SO_4^{2-} isotope concentrations (Wadham et al., 2004) and slope coefficients in regression
63 equations (Tranter et al., 2002) and geochemical modelling (Mitchell and Brown, 2008),
64 sulfide oxidation is a dominant geochemical control in many glacierised basins consisting of
65 various rock types. For example, pyrite and Fe-bearing oxides in bedrock may fertilize
66 subglacial biogeochemical processes (Mitchell et al., 2013), while the bulk mineralogy of

67 bedrock appears to play a second-order effect on chemical weathering in glacierised
68 catchments (Wadham et al., 2010b).

69 Several studies proposing that carbonation dominates chemical weathering reactions in
70 glacierised catchments rely on interpretations of major ions partitioned by chemical mass
71 balance stoichiometry (Sharp et al., 1995; Hodson et al., 2000; Hindshaw et al., 2011).
72 However, the relative importance of carbonation or sulfide oxidation as major H⁺ donating
73 processes vary widely in glacierised basins and is often related to small differences in
74 lithology (Singh and Hasnain, 2002; Krawczyk and Bartoszewski, 2008; Wadham et al.,
75 2010a). It is worth noting that some of these studies do not include simple hydrolysis in
76 reaction balancing (Hodson et al., 2000; Krawczyk et al., 2003; Krawczyk and Bartoszewski,
77 2008). Furthermore, chemical weathering in glacierised basins depends on many other factors
78 such as organic matter content, microbial processes, groundwater input, precipitation and
79 snowpack chemistry (e.g. Mitchell and Brown, 2008), all of which affect H⁺ donating
80 reactions.

81 In basins with valley-type glaciers, chemical weathering is mainly influenced by bulk
82 meltwater production and seasonal evolution of the subglacial drainage system. During the
83 early ablation season, differential leaching of snowpack-derived solutes (mainly Na⁺, Cl⁻)
84 dominates the chemical composition of the bulk meltwater and the contribution of solute from
85 geochemical weathering processes is low (Wadham et al., 2000; Yde et al., 2008; Stachnik
86 and Uzarowicz, 2011; Stachnik et al., 2014). At this time of year, subglacial conduits may be
87 blocked by ice or snow dams, preventing them from draining the glacier efficiently (Irvine-
88 Fynn et al., 2011). The breaking of these dams in combination with increased surface ablation
89 causes the occurrence of an early discharge peak during the early ablation season (Brown,
90 2002). As the ablation season progresses a more effective channelized drainage system is
91 developed, and the relative contribution from less efficient distributed subglacial drainage

systems with long water residence time diminishes (Irvine-Fynn et al., 2011). When the surface melt rate slows down during the late ablation season, the distributed subglacial drainage system again plays a more important role in recharging the subglacial channels (Nienow et al., 1998; Nowak and Hodson, 2014). In channelized (transport-dominated) systems, carbonation of carbonates and silicates generally predominates, whereas processes such as sulfide oxidation and organic carbon oxidation coupled to dissolution of silicates and carbonates are more important in distributed (weathering-dominated) systems (Tranter et al., 2002). This difference becomes evident during the late ablation season, where an increase in SO_4^{2-} compared to HCO_3^- has been attributed to sulfide oxidation coupled to carbonate or silicate dissolution in distributed systems (Wadham et al., 1998; Wadham et al., 2010b).

When glacial meltwater chemistry in the proglacial zone is compared to the chemical characteristics of subglacial outflows, the observed solute enrichment can be tied to biogeochemical processes operating in proglacial groundwater or in open channels (Cooper et al., 2002; Kristiansen et al., 2013). In the proglacial zone, biogeochemical processes are enhanced by the long residence time of near-surface water, slow groundwater flow, exposure of fresh rock surfaces due to glacier recession and high microbiological activity (Fairchild et al., 1999; Cooper et al., 2002; Bernasconi et al., 2011; Nowak and Hodson, 2014). Expanding vegetation cover provides organic acids and CO_2 from the oxidation of organic carbon, and this process subsequently facilitates chemical weathering (Egli et al., 2001; Kabala and Zapart, 2012; Vilmundardóttir et al., 2014). This may lead to an increase in solute fluxes of major ions (Ca^{2+} , Mg^{2+} , HCO_3^- , SO_4^{2-}) along proglacial transects (Wadham et al., 2001) and to an enhancement of chemical weathering of silicates (Mavris et al., 2012; Anderson 2006; Vilmundardóttir et al., 2014). Previous studies have shown that glacier forelands may account for 3-4 times more chemical denudation than the glacierised parts of basins (Anderson et al., 2000; Wadham et al., 2001).

Both oxic and anoxic sulfide oxidation coupled to carbonate and silicate dissolution have been observed in subglacial and proglacial zones (Cooper et al., 2002; Wadham et al., 2004; Wadham et al., 2007). The carbonation of both carbonates and silicates is likely to occur in both systems, but in the subglacial distributed system and in groundwater in the proglacial zone carbonation reactions may be related to microbial respiration processes (Tranter et al., 2002; Bernasconi et al., 2011), whereas the carbonation by atmospheric CO₂ sequestration occurs in open channels (Hodson et al., 2002). Sulfate reduction is recognised as a process observed exclusively in anoxic subglacial conditions (Wadham et al., 2007), whereas the dissolution of Ca-Mg sulfate, re-dissolution of precipitated calcite, CO₂ degassing during calcite precipitation and oxidation of organic carbon are geochemical processes operating in the oxygen-rich proglacial zone (Cooper et al., 2002; Bernasconi et al., 2011; Rutter et al., 2011; Vilmundardóttir et al., 2014). The effectiveness of silicate weathering in the proglacial area is still subject to debate as some studies indicate that an enhancement of the silicate weathering rate does occur (Anderson et al., 2000; Egli et al., 2001; Mavris et al., 2012; Kristiansen et al., 2013), whereas other studies neglect it (Wadham et al., 2001).

This study focuses on the characteristics and differences between chemical processes in subglacial and proglacial zones of the glacierised basin of Werenskioldbreen in Spitsbergen, High Arctic. First, we examine seasonal variations in the chemical processes throughout an entire ablation season and relate these to snow and ice ablation rates in the basin in relation to both the subglacial and proglacial drainage systems. Secondly, we assess the role of sulfide oxidation, carbonation and simple hydrolysis as dominant chemical weathering processes in these systems. Finally, we estimate solute fluxes and the chemical denudation rates and compare these to data from other glacierised basins worldwide. The results from this study provide new insights into the seasonal geochemical dynamics occurring in the glacial and proglacial environments of a highly reactive glacierised basin.

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143 **2. Study area**

144 Werenskioldbreen (77°05' N, 15°15' E) is located in Wedel-Jarlsberg Land, Southwest
145 Spitsbergen (Fig. 1). Its basin area covers 44.1 km², of which 27.4 km² are glacierised. The
146 glacier is 9.5 km in length and is a typical land-terminating, valley-type polythermal glacier of
147 this region of Svalbard (Hagen et al., 1993). The glacier elevation ranges from 60 to 650 m
148 a.s.l (Hagen et al., 1993) and the equilibrium line altitude (ELA) of the glacier is situated at ~
149 450 m a.s.l (Grabiec et al., 2012), although in the period 2009-2011 the ELA was above the
150 maximal altitude of glacier (Ignatiuk and Migala, 2013). The mean annual mass balance was -
151 0.43 m water equivalents during the period 1912-2005 (Grabiec et al., 2012). The maximum
152 glacier thickness is approximately 235±15 m (Ignatiuk and Migala, 2013), consisting of a 50-
153 100 m thick surface layer of cold ice with temperate ice below (Pälli et al., 2003). At the ~50
154 m thick snout, the glacier is frozen to the underlying bedrock and this cold-based zone
155 extends to a distance of 0.7–1 km up-glacier (Pälli et al., 2003).

156 The glacier drainage system consists of supraglacial streams draining into moulins and
157 a subglacial reservoir with bulk meltwater emerging from a few subglacial outflows at the
158 front (Pulina et al., 1999a). Four moulin systems have been observed to survive for more than
159 one ablation season: Lipertaven, Kvisla Cave and those below Eimfjellet and
160 Glasiologknausen; all other moulins are closed after a single ablation season due to ice
161 deformation (Rehak et al., 1990). The drainage system of Werenskioldbreen is subject to
162 interannual variability as observed by migration of the positions of subglacial outflows (Pälli
163 et al., 2003). In the years 1983, 1986, 1988 and 1993, the main outflow was situated at the
164 northern part of the glacier front (emerging at Kvisla) and minor outflows were situated in the
165 central part (Krawczyk and Opolka-Gądek, 1994). This configuration changed in the years
166 1998, 2007 and 2008, where the main outflow shifted position to the central part of the glacier

front (Pulina et al., 1999a; Kies et al., 2011; Szyrkiewicz et al., 2013). For 2010-2012, the main outflow was situated at the northern part of the glacier again, where the river Kvisla emanates (Piechota et al., 2012). Subglacial outflows with sub-artesian features (Black spring and Dusan outflows) have been observed tens of meters in front of the central part of the glacier terminus (Głowicki, 1982).

3. Geology and mineralogy within the Werenskioldbreen basin

Geologically, Werenskioldbreen is underlain by the Caledonian Hecla Hoek succession formed in the contact zone between three Proterozoic tectonic blocks (Czerny et al., 1993): 1) the Eimfjellet group, consisting of amphibolite, quartzite and chlorite schist is situated beneath its southern part, 2) the Deilegga group beneath the eastern part of the glacier, comprised mainly of phyllites with quartzite and silt intercalations, and calcareous and chlorite schists (Kieres and Piestrzynski, 1992), and 3) the Jens Erikfjellet formation including the Sofiebogen group in the north-western part of the basin, composed of greenschists, and muscovite-carbonate-quartz or carbonate-chlorite-quartz schists. The proglacial area belongs to the Sofiebogen and Eimfjellet groups, where mica-carbonate-quartz and grey calcite marbles dominate (Czerny et al., 1993). The Elveflya formation belongs to Sofiebogen group and consists of similar rocks (Czerny et al., 1993) and pyrite accompanied by pyrrhotite, galena, sphalerite, magnetite and haematite are the most common ore minerals. The carbonate minerals are present as siderite, ankerite or Fe-calcite, and occur in the Deilegga and Eimfjellet groups (Czerny et al., 1993).

The mineral compositions of the bedrock, proglacial sediments and suspended sediments are summarised in Table 1. Along a chronosequence from recently uncovered sediment in front of the glacier to sediment exposed ~80 years ago, exchangeable Ca decreases more than other exchangeable major ions (Mg, Na, K). In addition, dolomite and

amphibolite contents and the ratio of chlorite:mica decrease and formation of secondary minerals is unlikely (Kabala and Zapart, 2012). The suspended sediment consists of magnesium chlorite, feldspars, muscovite, quartz, calcite, and dolomite (Bukowska-Jania, 2007). Despite a low proportion of calcium carbonate in the bedrock, calcium carbonate comprises more than 7% of the proglacial sediment mineralogy, partly due to precipitation of calcite from water in subglacial tills (Bukowska-Jania, 2007).

4. Methodology

4.1. Field methods

Field investigations in the basin of Werenskioldbreen were carried out from May 12th to September 25th 2011. Discharge measurements at the hydrometric station (Fig. 1), and water sampling and meteorological measurements on the glacier surface were performed in Werenskioldbreen basin.

Variations in water level were measured at the hydrometric station at the bank of the Breelva river, which is incised into the bedrock at the Little Ice Age moraine, approximately 1.6 km from the glacier front (point 4, Fig. 1). Water level was measured at 10-minute logging intervals using a Mini-Diver probe and corrected for atmospheric pressure using a BaroDiver probe (both made by Schlumberger). At the beginning of the ablation season, when the riverbanks were covered by thick layers of snow, water velocity was determined by the salt dilution method (Rantz, 1982). When water level increased, water velocity was measured with a Seba F1 current meter. Total runoff for the ablation season was calculated based on a 1-hour running average of water level and a rating curve. A lack of water level data for September 2nd-8th was due to technical problems with the Mini-Diver probe, and this period was supplemented with estimated discharge (Majchrowska and Cichała-Kamrowska, 2013; Majchrowska et al., 2015) obtained by using the Deterministic Modelling Hydrological

System (DMHS; Vinogradov et al., 2011). For detailed information on discharge measurements, including errors, we refer the reader to Majchrowska et al. (2015).

The majority of water samples were collected from the hydrometric station twice per day at 6:00 and 18:00 UTC (N=183) from May 12th to September 25th. In addition, opportunistic sampling was conducted from the subglacial outflows: Kvisla main (N=28) from May 12th to September 25th, Dusan (N=24) from August 30th to September 25th, and Black spring (N=22) from August 21st to September 20th. Meltwater samples of supraglacial streams on the glacier surface were collected whenever possible (N=7). Between August 21st and September 25th samples were collected from a precipitation gauge situated in the vicinity of the hydrometric station (N=6) to supplement precipitation samples collected at the Polish Polar Station (PPS, ~16 km south of Werenskioldbreen) in Hornsund (N=31) from May 1st to September 30th. It was not possible to collect precipitation on Werenskioldbreen itself during the entire ablation period, so the precipitation chemistry is taken from samples collected at the PPS and analyses of precipitation chemistry are performed there throughout the entire year. Only precipitation samples with a charge balance error (CBE, Eq. (1)) below 30%, which are considered to show data unaffected by post-depositional processes such as evaporation, are reported in this article. We include precipitation samples from May 1st to May 12th as the ablation rate was low during this period (Majchrowska and Małarzewski, 2011) and solutes were assumed to accumulate within the snowpack.

$$CBE = \frac{(|\sum X^+ - \sum X^-|)}{(\sum X^+ + \sum X^-)} * 100\% \quad (1)$$

Where X^- - ion concentration in meq L⁻¹ in sample,

$\sum X^-$ - sum of anions in meq L⁻¹ in sample,

$\sum X^+$ - sum of cations in meq L⁻¹ in sample.

From July 17th to September 25th, the pH of water samples was determined *in situ* using a portable multi-parameter Hanna Instrument 9828, performed according to the USGS manual (Gibs et al., 2007). The accuracy and precision of the pH measurements were ± 0.02 and 0.01, respectively.

4.2. Ablation rate

The ablation rate was calculated by converting the energy available for melt into water equivalents. The daily energy at the glacier surface available for melt has been previously calculated using an energy balance model (Ignatiuk, 2012), factoring in the meteorological parameters air temperature, air humidity, radiation balance and wind speed from two automatic weather stations located on the surface of Werenskioldbreen. The ablation rate for the entire season was calculated by summing the daily melt. The model results were validated by observed melt rates obtained from a sonic ranging sensor SR-50, patterns of snow-line retreat, mass balance calculations and proglacial discharge. Observed ablation from the SR-50 and modelled ablation had a coefficient of determination of $R^2 = 0.99$ (Ignatiuk, 2012).

4.3. Laboratory methods

All water samples were vacuum-filtered immediately after collection using a Millipore filtration system with 0.45 μm pore size Whatman nylon filters. The samples were subsequently stored in pre-rinsed 250 ml HDPE bottles in cold, dark conditions (at a temperature of $\sim 4^\circ\text{C}$). The analyses of alkalinity and ion concentrations were performed within a few weeks after sampling at the hydrochemical laboratory at the PPS.

Filtered water samples were analysed for the concentrations of cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and anions (SO_4^{2-} , Cl^-) by ion chromatography (IC) at the PPS. Acidified samples were analysed for cation concentrations using an ion chromatograph Metrohm Compact IC

761 with a Metrosep C4–150/4.0 column with Tartaric acid/Dipicolinic acid eluent. The anions were determined using a Metrohm Compact IC 761 with a Metrosep C4–150/4.0 column and suppressor mode with a $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ eluent. Detection limits of the ion chromatography analyses for Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-} , Cl^- and NO_3^- were $0.5 \mu\text{eq L}^{-1}$, $0.8 \mu\text{eq L}^{-1}$, $0.4 \mu\text{eq L}^{-1}$, $0.3 \mu\text{eq L}^{-1}$, $0.2 \mu\text{eq L}^{-1}$, $0.3 \mu\text{eq L}^{-1}$ and $0.2 \mu\text{eq L}^{-1}$, respectively. Most samples had NO_3^- concentrations below the detection limit and therefore this element was not included in the CBE calculations. The precision level of all analyses was 1%. Two reference samples (Analytical Reference Material Rain-97 and Reference Material No 409 (BCR-409)) were used to determine accuracy, which was usually below 10% for both reference samples. Accuracy was higher than 10% for Na^+ (12%), K^+ (18%) and Cl^- (22%) for analytical reference material Rain-97 and Mg^{2+} (12%) for reference material No. 409 (BCR-409).

Alkalinity (predominantly HCO_3^-) was determined by automatic titration using a Metrohm 702 SM Titrino and pH was measured simultaneously using a glass pH electrode Unitrode. The detection limit and precision of the alkalinity measurements were $10 \mu\text{eq L}^{-1}$. Samples for Si measurements were acidified with nitric acid and transported at low temperature to the Hydrogeological Laboratory at the University of Science and Technology in Krakow at $\sim 4^\circ\text{C}$ and analysed with a Perkin Elmer ICP-OES Plasm 40 spectrometer. The detection limit was $3.32 \mu\text{eq L}^{-1}$.

CBE calculations were applied as a control of the chemical analysis quality and were calculated according to Eq. 1. The ranges of CBEs for all sites are shown in Table 2.

As the study site is adjacent to the sea, correction of surface water chemistry for marine aerosols is necessary (corrected concentrations are marked by an asterisk). This was based on the principle of constant ratios between major ion concentrations and Cl^- in oceanic water, which are as follows: $\text{SO}_4^{2-}/\text{Cl}^- = 0.103$, $\text{Na}^+/\text{Cl}^- = 0.86$, $\text{K}^+/\text{Cl}^- = 0.019$, $\text{Ca}^{2+}/\text{Cl}^- = 0.038$, $\text{Mg}^{2+}/\text{Cl}^- = 0.195$ (Holland, 1978). As Cl-bearing minerals are absent in the rocks of

Werenskioldbreen, Cl^- is considered to be a conservative ion derived only from atmospheric input by dry or wet deposition of marine aerosols. Correction of sea-salts was calculated based on Eq. 2:

$$X^* = {}^{\text{total}}X - {}^{\text{total}}\text{Cl}^- (X/\text{Cl}^-)_{\text{seasalt}} \quad (2)$$

X^* - concentration of ion X corrected for seasalts

${}^{\text{total}}X$ – total concentration of ion X

${}^{\text{total}}\text{Cl}^-$ – total concentration of Cl^- ion in sample

$(X/\text{Cl}^-)_{\text{seasalt}}$ – ratio of ion X: Cl^- in seawater.

The sulfate mass fraction (SMF) was calculated using Eq. 3:

$$\text{SMF} = {}^*\text{SO}_4^{2-} / ({}^*\text{SO}_4^{2-} + \text{HCO}_3^-) \quad (3)$$

${}^*\text{SO}_4^{2-}$ - the concentration of sulfate, corrected for atmospheric input (in $\mu\text{eq L}^{-1}$),

HCO_3^- - the concentration of bicarbonates (in $\mu\text{eq L}^{-1}$).

4.4. Solute flux, precipitation load and chemical denudation computations

Solute fluxes were calculated by multiplication of discharge-weighted mean ion concentration and mean daily discharge and standardised for catchment area size. The chemical denudation rate was calculated by using both mean concentration and discharge-weighted mean concentration to estimate the mean ion concentrations. The chemical weathering intensity (CWI) was calculated by dividing the cation denudation rate ($\text{meq m}^{-2} \text{a}^{-1}$) by specific annual runoff (m a^{-1}) according to Krawczyk et al. (2003). Solute load from precipitation was calculated by using the sum of precipitation from the PPS and mean ions concentration and then by using a gradient of 19% per 100 m of altitude increase as suggested for glacierised basins in Svalbard by Nowak and Hodson (2013).

5. Results

5.1. Chemical characteristics of precipitation and supraglacial waters

To better understand the chemistry of surface water within the Werenskioldbreen basin, we first examined the precipitation chemistry from Werenskioldbreen and PPS (situated ~16 km to the south of Werenskioldbreen at Hornsund Fjord) to gain information on the local atmospheric deposition of solutes (Table 3). Due to lack of data coverage for Werenskioldbreen, we used data from the PPS because this dataset covers the entire ablation season. During the study period (May 1st – September 30th 2011), the total precipitation amounted to 250.3 mm at the PPS. Snowfall was only registered twice, on May 4th and May 26th.

Sodium ions in precipitation were derived primarily from seawater (Eq. (2)), whilst K^+ , Ca^{2+} , Mg^{2+} and SO_4^{2-} originated mainly from dust transport in the atmosphere (Table 3). Non-sea salts SO_4^{2-} and Mg^{2+} may be sourced from the dissolution of aged (reacted) sea salt that underwent reaction with the nitrogen and sulfur oxides during transport in the atmosphere, whereas Ca^{2+} , Mg^{2+} and K^+ of non-sea salt origin may come from the mineral dust particles generated by wind erosion and transport of rock/sediment particles (Geng et al. 2010). The precipitation chemistry in the Werenskioldbreen basin was generally in the same range as in Hornsund (Tables 3), but some deviations between mean ionic concentrations occurred. In the Werenskioldbreen basin, Mg^{2+} , Cl^- , Na^+ and K^+ concentrations were 2–3 times lower than at Hornsund, whereas SO_4^{2-} was similar in concentration and Ca^{2+} was 3 times higher. The chemical analyses of snowpack samples from two snow pit excavations on Werenskioldbreen showed that ionic ratios were very similar to the marine ratios: $SO_4^{2-}/Cl^- = 0.123$, $Na^+/Cl^- = 0.85$, $K^+/Cl^- = 0.016$, $Ca^{2+}/Cl^- = 0.051$, $Mg^{2+}/Cl^- = 0.18$.

Precipitation had higher concentrations of most ions, excluding Ca^{2+} , than supraglacial streams (Table 3, 4). The enhanced Ca^{2+} concentration in supraglacial streams may originate from dissolution of carbonate dust deposited on the glacier surface.

343

344 *5.2. Water chemistry at subglacial conditions*

345 All ion concentrations increased from the supraglacial stream to subglacial outflows (Kvisla,
346 Black spring, Dusan) by more than one order of magnitude. Magnesium and SO_4^{2-} showed the
347 greatest increases from supraglacial streams to the Kvisla subglacial outflow (from 5 to ~220
348 ueq L^{-1} and from 6 to ~240 ueq L^{-1} , respectively; Table 4), whereas Cl^- exhibited the lowest
349 increase. Mean concentrations of all ions (excluding K^+) in Kvisla were higher than in the
350 sub-artesian subglacial outflows (Black spring and Dusan, Table 4), but minimum
351 concentrations of Na^+ and K^+ were lower. The ratios of $\text{HCO}_3^-:\text{SO}_4^{2-}$ and Ca^{2+} concentrations
352 were also higher in Kvisla than in other subglacial outflows. However, the dissolved silica
353 concentration (SiO_2) was higher by a factor of 1.5 in both sub-artesian outflows than in
354 Kvisla. Water pH was similar in all subglacial outflows (pH 8.8-9.1) and substantially higher
355 than in supraglacial streams (pH ~5.5).

356

357 *5.3. Temporal trends of water chemistry at the hydrometric station*

358 At the hydrometric station, all ion concentrations increased proportionally from subglacial
359 outflows. From Kvisla main to the hydrometric station, the ion concentrations increased for
360 K^+ by a factor of 1.5, and for SO_4^{2-} and Mg^{2+} by a factor of 1.3. At the hydrometric station,
361 SiO_2 was lower than at the sub-artesian subglacial outflows (Dusan, Black spring).

362 Seasonal variations in water chemistry at the hydrometric station are shown in Table 5
363 and Fig. 2. We divided the ablation season into three periods: early ablation (12 May – 18
364 June 2011), peak flow (19 June – 10 September 2011) and late ablation (11 September – 25
365 September 2011) to account for pronounced changes in the water chemistry and discharge at
366 the hydrometric station between these periods. In mid-June, the transition from early ablation
367 to peak season was marked by an increase in discharge from $2.5 \text{ m}^3 \text{ s}^{-1}$ to more than $5 \text{ m}^3 \text{ s}^{-1}$,

and a decrease in ion concentrations. At the beginning of September, the transition from the peak flow season to the late ablation season was characterised by an increase in crustally-derived ions.

Early ablation season

During the early ablation season, a marked drop in the concentration of all ions occurred at the hydrometric station. Sodium and Cl^- decreased from $900 \mu\text{eq L}^{-1}$ to $300 \mu\text{eq L}^{-1}$, whereas SO_4^{2-} and Mg^{2+} fell from $700 \mu\text{eq L}^{-1}$ to $300 \mu\text{eq L}^{-1}$ (Fig. 2). By the end of May, the concentrations of Na^+ , Cl^- and Mg^{2+} had decreased substantially as a result of a rain event. The concentrations of Na^+ and Cl^- responded quickly to the discharge increase, while the concentrations of Ca^{2+} ($\sim 1100 \mu\text{eq L}^{-1}$) and HCO_3^- ($\sim 900 \mu\text{eq L}^{-1}$) declined to 600 and $700 \mu\text{eq L}^{-1}$, respectively. Ca^{2+} made the largest contribution to the cation total, usually exceeding 40%, while both Mg^{2+} and the sum of Na^+ and K^+ contributed over 20% each (Fig. 3). In terms of the anion composition, HCO_3^- showed a concentration above 40% of the total, whereas the other anions contributed approximately 20% (Fig. 3). In contrast to these decreases, the concentrations of SO_4^{2-} , HCO_3^- , Na^+ and Cl^- were at a relatively constant level during the early ablation season from May 18th to May 28th ranging from 600 to $800 \mu\text{eq L}^{-1}$ (Fig. 2).

Peak flow season

At the beginning of the peak flow season, discharge exceeded $5 \text{ m}^3 \text{ s}^{-1}$ corresponding to an increase in the rate of ablation (Fig. 2). During the initial period of moderate ablation between June 18th and July 7th, the ion concentrations remained similar to their values at the end of the early ablation season. Peaks in ion concentrations were noted for Ca^{2+} and HCO_3^- from June 23rd to 26th (Fig. 2); whereas the concentration maximums of Na^+ and Cl^- were observed from

June 26th to 30th (Figs. 2, 3) and Na⁺ and Cl⁻ exhibited elevated concentration levels from June 19th to July 7th (Fig. 4). These changes indicate a significant leaching of ions from snowmelt. The strongest inverse correlation between an ion concentration and discharge was observed for Na⁺ ($r < -0.70$). Increase in the ablation rate in the later part of the peak flow season caused a peak in discharge that exceeded 15 m³ s⁻¹. Ion concentrations decreased throughout this period due to dilution, reaching a minimum in mid-July. The concentrations of Na⁺, Cl⁻, Mg²⁺ and SO₄²⁻ dropped to below 200 µeq L⁻¹, whereas Ca²⁺ and HCO₃⁻ had concentrations ranging from 400 µeq L⁻¹ to 700 µeq L⁻¹. The reduction in the concentrations of Ca²⁺ and Mg²⁺ coincided with the increase in discharge (Fig. 5). From August 26th to September 11th the concentration ratio of SO₄²⁻ to Ca²⁺ and HCO₃⁻ increased. The water chemistry of the peak flow and late ablation seasons at the hydrometric station was similar to that of Kvisla, whereas the other subglacial outflows (Black spring, Dusan) are clustered in a separate group in the Piper diagram due to the total concentrations of Na⁺ and K⁺ exceeding 20% (Fig. 3).

Late ablation season

During the late ablation season, the ablation rate decreased by comparison to the preceding peak flow season and the concentrations of most ions increased (with the exception of the primarily snowpack-derived ions Na⁺ and Cl⁻). The increase in concentrations of SO₄²⁻ and Mg²⁺ was most pronounced (from ~ 200 µeq L⁻¹ to 500-600 µeq L⁻¹). The SMF was ~0.4, which was higher than that of the peak flow season, while the daily discharge ranged from 5 to 16 m³ s⁻¹ (Fig. 5). The contribution of SO₄²⁻ to the total anion concentration reached 40%, exceeding the proportion observed in the early ablation season (Fig. 3). Both SMF and Mg²⁺ were similar to the beginning of early ablation season (Figs. 2, 5), and the concentrations of Na⁺ and Cl⁻ remained below 100 µeq L⁻¹, resembling those of the peak flow season.

5.5 Seasonal solute fluxes and chemical weathering rates

The solute flux rates fluctuated between the seasonal periods of the ablation season (Table 6). Maximum solute flux rates were observed during the peak flow and late ablation seasons, exceeding $1000 \text{ kg day}^{-1} \text{ km}^{-2}$, whereas the observed solute flux rates during the early ablation season were three times lower. Mean daily fluxes of dissolved constituents during the entire ablation season were arranged in descending order of magnitude (in $\text{kg day}^{-1} \text{ km}^{-2}$): HCO_3^- (565.6) > Ca^{2+} (201.7) > SO_4^{2-} (193.9) >> Mg^{2+} (36.8) >> SiO_2 (8.5) > K^+ (7.2) > Na^+ (4.0). The fluxes of SO_4^{2-} , Mg^{2+} and SiO_2 reflected a clear and gradual increase from early to late ablation season by a factor of two or more. The proportion of non-sea salt SO_4^{2-} flux decreased throughout the ablation season from 8% to 2%. The most prominent seasonal increase in flux was noted for Na^+ exceeding one order of magnitude, whereas the Cl^- flux showed a nearly two-fold decline from early to late ablation season.

The solute yields at the hydrometric station and precipitation are shown in Table 7. The runoff, ablation and precipitation totals for the entire ablation season were estimated to be $80.6 \times 10^6 \text{ m}^3$, $49.8 \times 10^6 \text{ m}^3$ and $14.1 \times 10^6 \text{ m}^3$, respectively. The runoff and precipitation totals in the peak flow and late ablation seasons were 9% and 17% lower than the respective totals for the entire ablation season. The cationic denudation rate (CDR) was $1601 \text{ meq m}^{-2} \text{ yr}^{-1}$ based on the discharge-weighted ion concentration, whereas if the mean concentration is used for calculating the CDR, it was estimated to $1762 \text{ meq m}^{-2} \text{ yr}^{-1}$. The solute yields from the precipitation corrected for marine aerosols reached only $8 \text{ meq m}^{-2} \text{ yr}^{-1}$. The chemical weathering intensity (CWI) indices, calculated according to Krawczyk et al. (2003), were less than $1000 \text{ meq m}^{-3} \text{ yr}^{-1}$. We can assume that the combined denudation rate of the proglacial and subglacial areas measured at the hydrometric station was equal to sea-salt corrected solute yields because the proportion of solute yield delivered by rain was negligible (Table 7).

Solutes derived from snowmelt were calculated from the marine ratio and were excluded from total solute yields by sea-salt correction of water chemistry.

6. Discussion

Chemical weathering in glacierised catchments depends on reactions providing H^+ ions that dissolve mineral/rock surfaces, such as sulfide oxidation, carbonation, organic carbon oxidation and simple hydrolysis. Dissolution of silicate or carbonate minerals is coupled to these reactions (e.g., sulfide oxidation coupled to carbonate/feldspar dissolution, carbonation of carbonate/feldspar surface Eqs (4-7)). These coupled reactions affect the water chemistry of a solution by enriching it with ions resulting in altered ion ratios and different slopes and intercepts in linear regression equations. These reactions are particularly important for Werenskioldbreen as evidenced by the linear regression coefficients and scatterplots of ions (Table 8; Fig. 6). Sulfide oxidation coupled to carbonate dissolution (SOCD) has slope coefficients of 2.0 and 1.0 for ion associations with $[*Ca^{2+}+*Mg^{2+}]$ vs. $*SO_4^{2-}$ and $[HCO_3^-]$ vs. $*SO_4^{2-}$, respectively (Eq. (4); Tranter et al., 2002; Wadham et al., 2010a). Carbonation of carbonates is characterised by a slope coefficient of 1.0 for the ion association $[*Ca^{2+}+*Mg^{2+}]$ vs. HCO_3^- (Eq. (6)). Dissolution of Ca and Mg efflorescent salts favours an ion association $[*Ca^{2+}+*Mg^{2+}]$ vs. $*SO_4^{2-}$ slope close to 1.0 (Eq. (8), Szyrkiewicz et al., 2013). Sulfide oxidation coupled to Na, K silicate dissolution causes increase in SO_4^{2-} concentrations leading to increase in the slope of the ion association $[*SO_4^{2-}]$ vs. HCO_3^- and decrease in the slope of the ion association $[*Ca^{2+}+*Mg^{2+}]$ vs. $*SO_4^{2-}$ (Eq. (5)). Also, Tranter et al. (2002) suggested that intercepts of $220 \mu eq L^{-1}$ in ions associations $[*Ca^{2+}+*Mg^{2+}]$ vs. $*SO_4^{2-}$ and $[HCO_3^-]$ vs. $*SO_4^{2-}$ indicate simple hydrolysis of carbonate at the initial stage of water contact with subglacial sediments (Eq. (9)), whereas higher intercepts indicate additional chemical reactions forming H^+ ions such as organic carbon oxidation (Eq. (10)). In case of simple

hydrolysis of silicate, concentrations of cations and OH^- increase (pH increases) but intercepts remain unchanged (Eq. (11)).

Equation 4. Sulfide oxidation coupled to carbonate dissolution (SOCD)

Equation 5. Sulfide oxidation coupled to silicate weathering (SOSW)

Equation 7. Carbonation of feldspar surfaces (albite/microcline – orthoclase)

Equation 8. Dissolution of gypsum (an example of efflorescent salts)

Equation 9. Simple hydrolysis of carbonate

Equation 10. Oxidation of organic carbon

Equation 11. Simple hydrolysis of feldspar

A SMF (calculated from Eq. (3)) equal to 0.5 corresponds to predominating SOCD (Eq. (4)). Carbonation of carbonates decreases SMF below 0.5 due to excess of HCO_3^- (Eq. (6)), whereas SMF increases above 0.5 for SOSW due to SO_4^{2-} excess (Eq. (5)), carbonate precipitation and Ca and Mg efflorescent salt dissolution (Eq. (8)) (Cooper et al., 2002; Tranter et al., 2002).

6.1. *Evolution of meltwater chemistry during the ablation season (hydrometric station)*

Meltwater in the ablation season of 2011 in Werenskioldbreen basin exhibited three periods of distinct characteristics: early ablation, peak flow and late ablation. During May, low ablation rates associated with high ion concentrations indicated leaching of ions from the snowpack in combination with release of solute-rich meltwater stored in the subglacial drainage system throughout the winter season (Fig. 2). The release of subglacial water by breaking dome-shaped naled ice formed in front of Werenskioldbreen increased ion concentrations (Krawczyk and Wach, 1993; Pulina et al., 1999b; Yde et al., 2012) during this period as well, and concentrations are apparently further augmented by brine exclusion during freezing in the early ablation season (Pulina, 1984). Meltwater during the late ablation season could endure the winter in the form of ice and liquid water stored in the glacier drainage system. In the following early ablation season this meltwater may contribute to high concentrations of crustally derived ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , SO_4^{2-}) and low concentration of dissolved sea-salts (Na^+ , Cl^-). However, we observed excess Na^+ and Cl^- in the early ablation season and at the beginning of the peak flow season, indicating that there is leaching of sea salts that accumulated in the snowpack throughout the winter.

On May 28th, a short period of rain and positive air temperature caused a hydrochemical regime shift in runoff from the basin. The large volume of water created by this event diluted the concentrations of all ions at the hydrometric station. A similar drop in ion concentrations at the transition from the early ablation season to the peak flow season was observed at the subglacial outflows of Werenskioldbreen in 1986 (Krawczyk, 1992). However, the decrease we observed was disproportionally distributed between particular ion groups. After a short decrease, the concentrations of Ca^{2+} and HCO_3^- increased to above 700 $\mu\text{eq L}^{-1}$ after June 7th, possibly due to the dissolution of pure calcite. Furthermore, in the early ablation season high input of ablation waters and the absence of an efficient subglacial

drainage network probably enhance calcite dissolution in the proglacial area. Recrystallisation of calcite has also been shown to increase the content of CaCO_3 in the proglacial sediments of Werenskioldbreen by 47% (Bukowska-Jania, 2007), and aerated waters reaching the subglacial system and proglacial groundwater could promote the processes of carbonation of CaCO_3 via atmospheric CO_2 (Tranter et al., 2002). However, slope coefficients of ion associations [$\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. HCO_3^-] and [$\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. SO_4^{2-}] were ~ 2.1 and ~ 1.7 , respectively, and the correlation coefficient for these ion associations exceeded 0.9, indicating that SOCD is more likely to occur than carbonation of carbonates (Table 8, Fig. 6).. These results reveal a dominance of SOCD during the early ablation season. This is supported by the fact that both snowmelt-saturated groundwater in the proglacial zone and aerated water in the subglacial drainage system contribute to enhance sulfide oxidation in the catchment. Also, pronounced sulfide oxidation results from subglacial meltwater storage during the accumulation season (Wadham et al. 2001). Furthermore, in the early ablation season the release of Ca^{2+} is related to SOCD (preferentially calcite) dissolution and the release of old waters from storage suggesting that dissolution of atmospheric CO_2 appears to play a minor role in chemical weathering processes.

The results also indicate that SOCD only partly explains chemical weathering during the early ablation season because slope coefficients differ from the theoretical stoichiometric coefficients (Eq. (4)). Excess SO_4^{2-} resulted in a slope coefficient of ~ 0.6 in ion association [HCO_3^- vs. SO_4^{2-}] and a slope coefficient of [$\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. SO_4^{2-}] lower than 2.0, both of which suggest an additional source of sulfate (i.e. Ca-Mg efflorescent salt, dissolution of sulfur bearing minerals accumulated in the snow, and SOCD). The slope and correlation coefficient of the ion association [HCO_3^- vs. SO_4^{2-}] were lowest during the early ablation season, indicating that multiple reactions dominated in the proglacial zone. SOSW could also result in an excess of SO_4^{2-} and explain the decrease of these slopes because total fluxes of

ions derived from the dissolution of silicates (Na^+ , K^+) were lower by a factor of ten than carbonate ions (Ca^{2+}). However, increase of silicate-derived ions and sulfate fluxes suggest that SOSW increased in importance throughout the ablation season.

The maximum discharge in July was caused by the rapid melting of the snowpack in the basin following another air temperature increase and rain event (9th July). Preceding this rapid melting of the snowpack, an period of high Na^+ and Cl^- concentrations at the end of June occurred along with increased snowmelt and coinciding with the retreat of the snowline to 200 m a.s.l. (Ignatiuk, 2012). The high concentrations of HCO_3^- and Ca^{2+} preceding this period signalled the late stage of naled ice degradation and the release of stored water from the winter reservoir (Fig. 2). The subsequent pronounced increase in the concentrations of Na^+ and Cl^- ions indicate the melting of naled ice and snow. Concentrations of other ions related to dissolution of rocks (Ca^{2+} and Mg^{2+}) appear to remain stable, suggesting that the hydrochemical switching is in agreement with the hydrological change in the glacier basin. A shorter response time of the discharge for air temperatures and precipitation events during high ablation also suggests that an ongoing development of an efficient subglacial drainage system is occurring. At the same time, the difference between the sum of Ca^{2+} and HCO_3^- and the sum of SO_4^{2-} and Mg^{2+} increased along with rising discharge (Fig. 2, Table 5). This may be attributed to suspended sediments which are present in high concentrations at this time and are highly reactive due to their high surface area (Anderson, 2005; Anderson, 2006). Laboratory experiments on freshly comminuted glacial flour (Brown et al., 1994; Brown et al., 1996) together with field data (Hallet et al., 1996; Anderson, 2006; Fairchild et al., 1999) suggest an enrichment of Ca^{2+} and HCO_3^- by carbonation of suspended sediments in open channels in the proglacial area or in subglacial conduits. The prominent decrease in the slope of the ion association [$\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. HCO_3^-] from early ablation season to late ablation season suggests carbonation. However, the slope of the ion association [HCO_3^- vs. SO_4^{2-}] is

close to 1.0 revealing a predominance of sulfide oxidation coupled to carbonate dissolution (SOCD), which operates under subglacial conditions and also in the proglacial zone. Nevertheless, the low correlation coefficient at peak flow ($r < 0.8$) shows that multiple processes including sulfide oxidation coupled to carbonate dissolution and carbonation of carbonates affected the water chemistry. During the peak flow season, two processes controlled the chemical weathering: at first melting of both the icings and snow, and subsequently sulfide oxidation in combination with carbonation of carbonates.

The late ablation season can be distinguished from the peak flow season by the rapid increase of ion concentrations that appeared on 11th September. The flux of crustally derived ions such as SO_4^{2-} , Na^+ , Mg^{2+} and total dissolved solids corrected for atmospheric input increased during the late ablation season (Table 6). A decreasing ablation rate in the basin reduces the dilution of solute by meltwater, resulting in favourable conditions for mineral dissolution in the proglacial zone and beneath the glacier.

Intercepts of the ion associations [HCO_3^- vs. SO_4^{2-}] and [$Ca^{2+}+Mg^{2+}$ vs. SO_4^{2-}] were ~2 times higher than 220 ueq L^{-1} (ranging from 418 to 447 ueq L^{-1}) during early ablation and peak flow seasons, suggesting that simple hydrolysis is accompanied by additional processes at initial stage of chemical weathering. Organic carbon oxidation can lead to the rise of the intercept of these regression equations by delivering H^+ that dissolves carbonates (Tranter et al., 2002). However, compared to other glacierised basins the organic carbon pool (5 g kg^{-1}) in the sediments at our site is rather low with a low increasing gradient along the chronosequence (Kabala and Zapart, 2012). Thus, it is likely that organic matter oxidation has a limited influence on the water chemistry of Werenskioldbreen. Nevertheless, the thick sediment cover in proglacial zone may promote the microbial production of CO_2 leading to higher intercepts for ion associations [HCO_3^- vs. SO_4^{2-}] and [$Ca^{2+}+Mg^{2+}$ vs. SO_4^{2-}] (Fig. 6, Table 8, Wadham et al. 2010). Alternatively, re-dissolution of calcite rich proglacial

sediment, driven by atmospheric CO₂, is another potential explanation for elevated intercepts. Proglacial calcite precipitation may lead to high content of calcite (up to 47%) in the vicinity of naled ice assemblages (Bukowska-Jania, 2007) and thereby be a significant source of HCO₃ and *Ca²⁺, particularly during the early ablation and peak flow seasons.

There is increasing chemical weathering along the chronosequence due to increasing vegetation cover, and the results indicate that divalent ions (especially Ca²⁺) are leached more readily than monovalent ions (primarily Na⁺), in agreement with previous studies (Moulton et al., 2000; Egli et al., 2001; Mavris et al., 2010). Therefore, divalent ions are rapidly depleted from the sediments close to the glacier front. Similarly, Kabala and Zapart (2012) observed a decreasing trend in exchangeable Ca²⁺ from younger sediments freshly uncovered in front of the glacier to 80 year-old soils in the proglacial area of Werenskioldbreen. An increase of the cation exchange capacity along chronosequences from freshly exposed sediment to older proglacial soils has also been observed (Bernasconi et al., 2011). Organic matter content increase is related to vegetation, and enhanced silicate weathering may be responsible for an increase of ion exchange capacity in older soils (Egli et al., 2001; Egli et al., 2006; Mavris et al., 2010; Mavris et al., 2012). Silicate weathering may lead to formation of secondary minerals in the proglacial area such as allophane, illite or kaolinite (Yde et al., 2005; Mavris et al., 2010; Vilmundardóttir et al., 2014). Although silicate weathering, organic matter content and vegetation cover area increase in the proglacial area of Werenskioldbreen (Piroznikow and Gorniak, 1992; Kabala and Zapart, 2012), the chemical weathering rate is still low due to the short time of 80 years since deglaciation (Kabala and Zapart, 2012). There is also no direct evidence of secondary clay mineral formation in the proglacial area of Werenskioldbreen, although the contents of silicate minerals such as amphibolite and mica decrease along the chronosequence (Kabala and Zapart, 2012). Additionally, soil pH

decreases from younger to older sediments due to decay of plant residues (Kabala and Zapart, 2012).

6.2. Chemical weathering under subglacial conditions

At Kvisla, the regression slopes for the ion associations [$\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. SO_4^{2-}], [HCO_3^- vs. SO_4^{2-}] and [$\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. HCO_3^-] (Table 8, Fig. 6) are close to the theoretical slopes of sulfide oxidation coupled to carbonate dissolution and far from the slope for carbonation (Tranter et al., 2002). The lack of outliers in the regression and the strong correlations exceeding $r=0.9$ in all ion associations indicate that sulfide oxidation coupled to carbonate dissolution prevailed during the ablation season. Interestingly, Kvisla appears to be sourced from a channelised system, where carbonation by atmospheric CO_2 due to turbulent flow is expected to dominate (Mitchell and Brown, 2008). However, since sulfide oxidation coupled to carbonate dissolution prevails, the water at Kvisla must be primarily derived from a distributed drainage system with long residence time of water and high rock-to-water ratio. Similar controls have previously been invoked to explain changes in water chemistry in a channelised system during a high ablation event (Lamb et al., 1995). Hydrogeological modelling by Piechota et al. (2012) showed that Kvisla collects the ablation water from many small tributaries. Also, high ^{222}Rn concentrations in the main outflows showed a long residence time of meltwater in subglacial sediment, without atmospheric contact (Kies et al., 2011).

The Dusan outflow exhibits slopes different from sulfide oxidation coupled to carbonate dissolution, indicating the occurrence of additional chemical processes (Table 8, Fig. 6). The slopes of ion associations [$\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. HCO_3^-] (~ 2.0) and [HCO_3^- vs. SO_4^{2-}] (~ 1.3) reveal the dominance of sulfide oxidation coupled to dissolution of carbonates occurring along the flow path of the Dusan outflow. Nearly 30% excess of HCO_3^- over SO_4^{2-}

in the former ion association suggests that an additional process enriched the water with HCO_3^- . Microbial respiration enriching water in CO_2 under slow water flow conditions, as proposed by Wadham et al. (2010), seems insufficient to explain the significant excess of HCO_3^- observed here. The outflow regime in the vicinity of Dusan is characterised by a quick response to ablation and high precipitation events (Krawczyk, 1992) and hence the turbulent flow hinders microbial respiration. The excess of HCO_3^- and the slope of the ion association [$*\text{Ca}^{2+} + *\text{Mg}^{2+}$ vs. HCO_3^-] close to 1.0 support the occurrence of carbonation as an additional chemical reaction. The short flow path in the central part of the glacier favours the potential for carbonation. Another possible explanation of the slope of [$*\text{Ca}^{2+} + *\text{Mg}^{2+}$ vs. HCO_3^-] is an ion exchange that leads to a decrease in divalent ions compared to monovalent ions. The concentrations of $*\text{Ca}^{2+}$ and $*\text{Mg}^{2+}$ were lower than at other sites (Fig. 6), whereas the concentrations of Na^+ and K^+ were higher (Table 4). As the local bedrock consists of silicate minerals (i.e. albite) (Czerny et al., 1992; Czerny et al., 1993), ion exchange and silicate weathering are likely processes.

High SiO_2 concentration compared to other sites suggests enhanced chemical weathering of silicates (Table 4). However, it is difficult to distinguish between the relative importance of each process because both microbial respiration and ion exchange can lower the concentrations of divalent ions. Nevertheless, the high ratio of exchangeable Ca:Na in recently exposed sediments from Werenskioldbreen observed by Kabala and Zapart (2012) indicates a high ion exchange capacity. Ion exchange affects the water chemistry significantly in other glacierized basin as well (e.g. Graly et al. 2014, Wadham et al. 1998). Despite the dominance of sulfide oxidation, the short residence time of water in the subglacial upwelling system favours additional reactions such as carbonation and ion exchange occurring along the flow path. This interpretation contradicts with the common assumption that proglacial

upwellings are connected to a drainage system with long residence time of water and limited carbonation by atmospheric CO₂ (Wadham et al., 2010a, b).

The Black spring showed the lowest slopes for all ion associations (Fig. 6, Table 8). Despite of a slope of ~0.9 for the ion association [HCO₃⁻ vs. *SO₄²⁻] that suggests sulfide oxidation coupled to carbonation of carbonates, the slope of [*Ca²⁺+*Mg²⁺ vs. *SO₄²⁻] below 1.4 indicates the presence of additional geochemical weathering processes. These are most likely due to carbonation, Ca and Mg efflorescent salt dissolution, simple hydrolysis and oxidation of organic matter. Although the slope of the ion association [*Ca²⁺+*Mg²⁺ vs. HCO₃⁻] is close to the level expected for carbonation, the slope of the ion association [HCO₃⁻ vs. *SO₄²⁻] is close to 1.0 indicating sulfide oxidation coupled to carbonate dissolution (Lamb et al., 1995). However, the surplus of SO₄²⁻ could be partly explained by the dissolution of Ca and Mg efflorescent salts, a process that would lower the slope of ion association [*Ca²⁺+*Mg²⁺ vs. *SO₄²⁻] towards 1.0. Sulfuric acid provided by from sulfide oxidation dissolves Ca-Mg efflorescence salts. Low correlation coefficients (r < 0.8) compared to subglacial outflows confirmed that multiple reactions control the chemical composition. Also, quick flow (Piechota et al., 2012) and a large channel size (2-3 m wide) after 25 years of functioning exhibit conditions of turbulent flow favouring carbonation accompanied by Ca and Mg efflorescent salt dissolution.

6.3. Solute fluxes and chemical denudation

During the peak flow and late ablation seasons the mean daily solute fluxes were high in comparison with the early ablation season (Table 6), due to the close relation between discharge and solute fluxes. From the early ablation season to the late ablation season the daily fluxes of *SO₄²⁻, *Mg²⁺, *Na⁺ and *K⁺ increased significantly. Total fluxes during peak flow and late ablation were similar to Ebba River (Szpikowski et al. 2014). The fluxes of Ca²⁺

and HCO_3^- were relatively stable between the peak flow and late ablation seasons. Rapid release of Ca^{2+} and HCO_3^- from the surface of suspended sediments has been reported by Brown et al. (1996) and Gíslason et al. (2006) and induced the highest load of these ions during the peak flow season (Table 6). From the early ablation season to the peak flow season the yields of Ca^{2+} and HCO_3^- increased by a factor of 3-4, the concentration of $^*\text{Ca}^{2+}$ decreased by a factor of two at the highest discharges, and $^*\text{Mg}^{2+}$ showed a five-fold decline (Fig. 5). Also, modest decreases in Ca^{2+} and HCO_3^- were observed compared to other ions (Table 5). These changes are in accordance with the low slope of ion association [$^*\text{Ca}^{2+} + ^*\text{Mg}^{2+}$ vs. HCO_3^-] at the peak flow season, although the rates of HCO_3^- and Ca^{2+} release from suspended sediments vary depending mostly on the discharge.

The fluxes of many ions ($^*\text{SO}_4^{2-}$, $^*\text{K}^+$, $^*\text{Na}^+$ and $^*\text{Mg}^{2+}$) showed a pronounced increase during the ablation season (Table 6). The vast amount of ablation water dilutes solutes sourced from the most active sites of chemical weathering (groundwater in the proglacial area or meltwater in the distributed subglacial system). Increase in the $^*\text{Na}^+$ and $^*\text{K}^+$ fluxes can be attributed to the enhancement of chemical weathering of silicates or ion exchange, which takes place as a consequence of long residence time of meltwater and high rock:water ratio (e.g. Tranter et al., 1993; Anderson, 2005; Hindshaw et al., 2014). During the early ablation season, hydrogen ions released from snowmelt may be exchanged for divalent cations (Clow and Mast, 2010). When the amount of snowmelt abates, ion exchange on the silicate minerals surfaces releases Na^+ and K^+ to the solution and adsorbs divalent ions on the exchange surface (Table 6). Despite being within the range of the previously noted sulfate fluxes by Szyrkiewicz et al. (2013), our results show a clear seasonal increase of sulfate fluxes that suggests increasing sulfide oxidation along with ablation season progress. Sulfide oxidation is known to be a donor of H^+ to the chemical weathering of silicates and carbonates. This is in accordance with the results showing that the fluxes of the silicate-derived ions

(*Na⁺, *K⁺) are considerably lower than carbonate-sourced ion (*Ca²⁺). Simultaneous release of ions and dissolved silica is often related to chemical weathering of silicates (Tranter et al, 2002), but the flux of *Mg²⁺ is higher than the dissolved silica flux (Table 6). This could be explained by incongruent chemical weathering of silicates, which form secondary minerals (i.e. kaolinite, Eq. (5)) or weathered silicate surfaces (Eq. (11)). Alternatively, dissolved silica flux could be related to the dissolution of Na-K bearing silicates (i.e. albite or muscovite). Nevertheless, a high load of dolomite transported as suspended sediments and pronounced leaching of dolomite in the proglacial area indicate that the dissolution of dolomite is a major source of *Mg²⁺ (Bukowska-Jania, 2007; Kabala and Zapart, 2012).

The CDR of 1601 meq m⁻² yr⁻¹ in the Werenskioldbreen basin is considerably higher than in other glacierised basins in Svalbard (Hodson et al., 2000). The previous comprehensive work from Werenskioldbreen on the chemical denudation is from 1979-1980 and 1986 (Pulina et al., 1984; Krawczyk et al., 2003) and revealed ~25% and ~18% lower denudation rates than was observed in 2011. Similar CDR have been found in glacierised basins situated in tectonically active areas in the Himalayas (Batura Glacier 1560 meq m⁻² yr⁻¹ (Collins et al., 1996); Dokriani Glacier 4200 meq m⁻² yr⁻¹ (Hasnain and Thayyen, 1999)), in Iceland (Hvita-south Gulfos 1100 meq m⁻² yr⁻¹ (Gíslason, 1996)) and in Alaska (Worthington Glacier 1600 meq m⁻² yr⁻¹ (Anderson et al., 1997)). Conversely, chemical denudation rates below 500 meq m⁻² yr⁻¹ have been reported in Svalbard (Vatne et al., 1995; Wadham et al., 1998; Hodson et al., 2000; Yde et al., 2008) and the previous maximum CDR in the archipelago was 713 meq m⁻² yr⁻¹ in the Scottbreen basin (Krawczyk and Bartoszewski, 2008). This implies that the Werenskioldbreen basin is extremely active from a chemical denudation perspective and that chemical denudation in Svalbard could be higher than previously thought. However, the relatively high runoff from the Werenskioldbreen basin exceeds runoff at other study sites (Hodson et al., 2000). The specific annual runoff from

glacierised basins in Svalbard tends to be below 1 m (Hodgkins et al., 1997; Hodson et al., 2000; Yde et al., 2008), while in the Werenskioldbreen basin it exceeds 1.8 m (Table 7). It is therefore very likely that the high rate of chemical denudation is primarily due to high discharge and secondarily high chemical weathering rates. This assessment is supported by comparison to other glacierised basins in Svalbard with similar water chemistry composition (Wadham et al., 1997; Hodson et al., 2002; Szpikowski et al. 2014). When CDR is normalised by runoff, the Werenskioldbreen basin chemical denudation rate is only slightly higher than in other Svalbard basins. Similar runoff-normalised CDR was noted for Scottbreen (Krawczyk and Bartoszewski, 2008) and Longyearbreen (Yde et al., 2008). Solutes derived from snowmelt were calculated from the marine ratio and was excluded from total solute yields by sea-salt correction of water chemistry.

7. Conclusions

This work presents a hydrochemical, hydrological and ablation dataset covering an entire ablation season at Werenskioldbreen, a polythermal land-terminating glacier situated in Svalbard. The major findings show:

- higher chemical denudation rates than previously reported from Svalbard glaciers. This is primarily due to high rates of ablation and runoff rather than higher chemical weathering intensities. The rate of chemical denudation in the Werenskioldbreen basin in 2011 was among the highest recorded for a glacierised basin worldwide, reaching 1601 meq $\text{m}^{-2} \text{yr}^{-1}$ (or 121.9 t $\text{km}^{-2} \text{yr}^{-1}$). This was caused by a high specific annual runoff of 1.8 m, which enabled transport of a substantial amount of dissolved solutes;
- the first annual record from a glacierized catchment showing re-dissolution of calcite driven by atmospheric CO_2 during the early ablation and peak flow seasons, causing elevated concentrations of Ca^{2+} and HCO_3^- in the proglacial zone and high fluxes of Ca^{2+} and

HCO₃⁻ during the peak flow season. This also shows that organic matter oxidation may not play an important role in carbonate dissolution in young proglacial zones (~80 years). Throughout the ablation season, continuous leaching of calcium carbonate in the proglacial zone caused a drop in intercepts of the ion associations [HCO₃⁻ vs. *SO₄²⁻] and [*Ca²⁺+*Mg²⁺ vs. *SO₄²⁻] from between 418 and 447 µeq L⁻¹ to values typical for simple hydrolysis (220 µeq L⁻¹). Hence, the proglacial dissolution of calcium carbonate by atmospheric CO₂ may be more important to proglacial solute fluxes than biological activity;

- that sulfide oxidation is a better parameter for determination of the drainage system configuration for small polythermal glacier (short water residence time when compared to large glacier and ice sheets) than the previously used concentrations of Na⁺ and K⁺. Sulfide oxidation coupled to dissolution of carbonates dominates in the distributed subglacial drainage system characterized by long flow paths. In contrast, silicate dissolution is related to the more discrete subglacial drainage system characterized by short flow paths. These findings contradict with the common assumption that relatively slow silicate weathering is related to distributed subglacial drainage systems.

Our study of Werenskioldbreen indicates that at small glaciers with relatively low water residence time and presence of sulfide and carbonate minerals, sulfide oxidation coupled with carbonate dissolution predominates. This is likely to be in contrast to larger glaciers, where sulfide oxidation coupled to silicate weathering becomes important.

Future progress should focus on advancing our understanding of the dynamics of chemical denudation in glacierised basin by coupling water chemistry with estimations of glacier ablation rates, runoff and subglacial storage. Water sampling should be performed more extensively during the early and late ablation seasons when elevated ion concentrations are observed.

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 1098 solute export from a Greenland Ice Sheet catchment, Watson River, West Greenland.
 1099 *J. Hydrol.* 519, 2165-2179.
 1100

1101 Table 1. Mineral composition of bedrock, proglacial sediments and suspended sediment in the
1102 Werenskioldbreen basin.

Major minerals	Position	Type of rock/sediments	Reference
Fe-dolomite, galena, pyrite, quartz, sphalerite	Outcrops in southern part of proglacial zone	Bedrock - massive sphalerite ore	Czerny et al., 1992
Ankerite, barite, Fe-dolomite, quartz	Outcrops in southern part of proglacial zone	Bedrock (southern part) - carbonate minerals from ore veins	Czerny et al., 1992
Albite, ankerite, chlorite, Fe-dolomite, muscovite, quartz	Outcrops in southern part of proglacial zone part	Bedrock (southern part) - muscovite-carbonate-quartz schists	Czerny et al., 1992
Chlorite, chloritoid, muscovite, paragonite, quartz	Outcrops in southern part of proglacial zone part	Bedrock (southern part) - chloritoid-bearing quartz mica schists	Czerny et al., 1992
Magnesium chlorite, feldspar, muscovite, quartz, calcite, dolomite	Hydrometric station	Suspended sediment in river	Bukowska-Jania 2007
Amphibolite, chlorite, dolomite, feldspar, mica	Southern part	Proglacial sediments	Kabala and Zapart, 2012
Quartz, quartz-feldspar or quartz-mica aggregates, quartzites and quartzose schists, chlorite schists, mica schists, marbles, quartzite conglomerates	Glacier portal at Kvisla	Pebbles glaciofluvially deposited	Kowalska and Soroka, 2008
Quartz, quartz-feldspar or quartz-mica aggregates, quartzites and quartzose schists, chlorite schists, marbles, quartzite conglomerates, amphibolites, gneisses	Subglacial outflows central part (vicinity of New and Black spring)	Pebbles glaciofluvially deposited	Kowalska and Soroka, 2008
Quartz-feldspar or quartz-mica aggregates, quartzites and quartzose schists, chlorite schists, mica schists, marbles, quartzite conglomerates, amphibolites	Southern part (Angell part)	Pebbles glaciofluvially deposited	Kowalska and Soroka, 2008

1103

1104

1105 Table 2. Charge balance errors of the chemical analysis for all sites in the Werenskioldbreen
 1106 basin and precipitation from Hornsund station.

Site	W	HRN	Supraglacial high	Black spring	Kvisla	New	HS
Mean	18.8%	10.0%	10.9%	3.1%	3.7%	2.7%	2.0%
Min	4.8%	0.6%	2.0%	0.8%	0.1%	0.1%	0.0%
Max	30.2%	29.9%	28.1%	5.7%	6.5%	5.9%	8.0%

1107 (HS) surface water at hydrometric station, and (W) precipitation data from hydrometric
 1108 station at the Werenskioldbreen and (HRN) Polish Polar Station at Hornsund.
 1109

1110 Table 3. Amount of precipitation and its chemistry. Samples were collected close to the

1111 Polish Polar Station in Hornsund.

		01.05-18.06.2011 (N=7) 42.5 mm (HRN)			19.06-10.09.2011 (N=17) 140.5 mm (HRN)			11.09-30.09.2011 (N=7) 67.3 mm (HRN)			01.05-30.09.2011 (N=31) 250.3 mm (HRN)			1.08-30.09.2011 (N=6) 131 mm (W)		
		Total	Marine	nss	Total	Marine	nss	Total	Marine	nss	Total	Marine	nss	Total	Marine	nss
HCO ₃ ⁻	min	0			0			0			0			0		
	mean	15			0			0			3			52		
	max	28			0			0			28			140		
SO ₄ ²⁻	min	13	5	5	1	1	0	4	1	3	1	1	0	8	1	5
	mean	42	11	30	24	15	9	20	12	8	27	14	13	15	5	10
	max	109	32	77	52	44	36	106	80	26	109	80	77	28	11	17
Cl ⁻	min	44			14			6			6			10		
	mean	111			151			121			135			50		
	max	311			430			772			772			108		
Ca ²⁺	min	4	2	0	0	0	0	0	0	0	0	0	0	7	0	7
	mean	14	4	9	13	5	8	6	5	2	12	5	7	23	2	21
	max	32	12	20	46	16	36	32	29	6	46	29	36	43	4	42
Mg ²⁺	min	6	9	0	0	0	0	0	0	0	0	0	0	0	0	0
	mean	21	22	1	31	29	3	21	22	0	26	26	2	13	9	3
	max	57	61	4	72	84	28	146	151	0	146	151	28	24	21	6
K ⁺	min	1	1	0	0	0	0	0	0	0	0	0	0	0	0	0
	mean	3	2	1	11	2	9	2	2	0	7	2	5	4	1	3
	max	4	4	2	120	6	117	15	15	0	120	15	117	10	2	8
Na ⁺	min	37	37	0	23	12	0	11	5	6	11	5	0	16	9	0
	mean	95	94	1	141	128	13	126	104	22	127	115	12	40	39	1
	max	258	258	2	389	370	37	757	664	93	757	664	93	87	87	9

1112 HRN - refers to precipitation collected at Polish Polar Station; W - refers to precipitation collected close
1113 to hydrometric station in vicinity of Werenskioldbreen; nss - denotes non-sea-salt concentration of
1114 ions.

1115 Table 4. Water chemistry from subglacial outflows (Black spring, New, Kvisla), the hydrometric station
 1116 and supraglacial high (Supra high) in the Werenskioldbreen basin. All concentrations, excluding pH, are
 1117 expressed in $\mu\text{eq L}^{-1}$.

	Black spring (N=22), pH (N=21)			Dusan (N=24), pH (N=20)			Kvisla main (N=34), pH (N=23), SiO ₂ (N=28)			HS (N=183), pH (N=78), SiO ₂ (N=86)			Supraglacial high (N=7)		
Species	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
pH	9.06	9.59	8.61	8.84	9.61	8.30	8.92	9.78	8.36	8.26	9.74	7.44	5.54	4.95	7.52
HCO ₃ ⁻	383	290	470	414	310	640	540	300	1170	666	450	1060	34	0	90
SO ₄ ²⁻	138	66	208	162	81	289	242	12	1020	317	85	811	6	1	16
Cl ⁻	76	43	104	76	40	124	119	9	931	214	28	991	25	4	44
Ca ²⁺	363	283	468	401	260	621	539	303	1524	734	444	1107	42	9	94
Mg ²⁺	89	56	123	101	54	201	219	20	860	263	87	598	5	0	17
Na ⁺	104	68	137	104	65	168	122	9	799	190	37	833	23	4	40
K ⁺	24	2	34	26	17	39	12	2	26	17	6	37	2	0	5
SiO ₂ [#]	16	8	69	15	2	45	10	2	30	10	2	34	b.d.	b.d.	b.d.

1118 b.d. – below detection; # - calculation of mean SiO₂ includes also SiO₂ below detection limit by assuming concentration at level 75%
 1119 detection limit.

1120

1121 Table 5. Water chemistry in different periods of the ablation season at the hydrometric station
 1122 in the Werenskioldbreen basin. All concentrations, excluding pH, are in $\mu\text{eq L}^{-1}$.

Species	HS early melt (N=57)			HS peak (N=100), pH(N=52), SiO ₂ (N=60)			HS end season(N=26)		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
pH	n.m.	n.m.	n.m.	8.38	9.36	7.96	8.08	9.74	7.44
HCO ₃ ⁻	704	480	890	626	475	900	738	450	1060
SO ₄ ²⁻	444	253	725	208	85	366	454	287	811
Cl ⁻	361	152	991	168	28	385	68	31	113
Ca ²⁺	844	558	1107	654	444	1084	799	558	1068
Mg ²⁺	375	243	598	186	87	297	314	182	549
Na ⁺	310	146	833	148	37	320	92	47	155
K ⁺	16	6	37	17	9	34	21	11	35
SiO ₂ [#]	n.m.	n.m.	n.m.	10	2	34	11	2	33

1123 n.m. – not measured; [#] - calculation of mean SiO₂ includes also SiO₂ below detection limit by
 1124 assuming concentration at level 75% detection limit.

1125

1126 Table 6. Mean daily fluxes of dissolved constituents expressed in $\text{kg day}^{-1} \text{km}^{-2}$ and mean daily
 1127 discharge in $\text{m}^3 \text{day}^{-1}$ at the hydrometric station during the ablation season.

Season part	Number of days sampled	Q [#]	HCO ₃ ⁻	*SO ₄ ²⁻	SO ₄ ²⁻	*Ca ²⁺	*Mg ²⁺	*Na ⁺	Na ⁺	*K ⁺	K ⁺	Cl ⁻	SiO ₂	TDS ^{##}
Early ablation	31	2.16	181	81	88	70	15	1	27	1	2	49	n.m.	347
Peak flow	54	8.81	659	158	173	224	32	4	59	9	12	103	10	1097
Late ablation	14	6.72	593	282	287	210	48	10	28	10	11	32	9	1163
Total	99	7.12	566	194	208	202	37	4	57	7	9	99	8	1018

1128 n.m. – not measured; [#]discharge data are available from May 23rd to September 30th 2011, ^{##}

1129 sum of dissolved solids fluxes corrected for marine input, bicarbonates and dissolved silica.

1130

1131 Table 7. Runoff, sum of precipitation, ablation rate and solute yields corrected and
 1132 uncorrected for marine input at the hydrometric station and solute load delivered with
 1133 precipitation in 2011 in the Werenskioldbreen basin. Denudation rates were calculated based
 1134 on: (DW) discharge-weighted concentrations (Hodson et al., 2000; Yde et al., 2014), (MC)
 1135 mean daily concentrations. Chemical denudation is calculated for entire ablation season
 1136 23.05-30.09 2011 when discharge data were available. (#) the cationic denudation rate (CDR).
 1137

Type of solute load	Note	Runoff or precipitation 10 ⁶ m ³	Ablation 10 ⁶ m ³	Specific runoff or precipitation m	HCO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	Chemical denudation or precipitation load t km ⁻² a ⁻¹	meq ⁺ m ⁻² a ⁻¹	CWI# meq m ⁻³ a ⁻¹
Entire corrected	DW	80.6	49.8	1.83	637	238	667	181	14	14	n.a.*	121.9	1601	876
Entire corrected	MC	80.6	49.8	1.83	665	289	722	217	13	13	n.a.*	132.2	1762	964
Entire uncorrected	DW	80.6	49.8	1.83	637	253	673	209	135	17	146	138.8	1888	1034
Entire uncorrected	MC	80.6	49.8	1.83	665	310	729	256	179	17	200	155.3	2157	1181
Precipitation	MC	14.1	n.a.	0.32	3	27	12	26	127	7	135	2.7	49	n/a

* - Cl⁻ is absent because ion concentrations are corrected for a sea salts based on the marine ratio.

1138

1139

1140 Table 8. Simple linear regression equations between major ions in glacial river water at the
1141 hydrometric station and in subglacial outflows of the Werenskioldbreen basin.

Ion association	Hydrometric station early ablation (N=57)	Hydrometric station peak flow (N=100)	Hydrometric station late ablation (N=26)
HCO ₃ ⁻ vs. *SO ₄ ²⁻	$y = 447 + 0.63 \cdot x$ ($r = 0.81, p < 0.001$)	$y = 439 + 0.98 \cdot x$ ($r = 0.76, p < 0.001$)	$y = 271 + 1.05 \cdot x$ ($r = 0.92, p < 0.001$)
*Ca ²⁺ + *Mg ²⁺ vs. *SO ₄ ²⁻	$y = 430 + 1.74 \cdot x$ ($r = 0.97, p < 0.001$)	$y = 418 + 2.00 \cdot x$ ($r = 0.83, p < 0.001$)	$y = 368 + 1.63 \cdot x$ ($r = 0.91, p < 0.001$)
*Ca ²⁺ + *Mg ²⁺ vs. HCO ₃ ⁻	$y = -352 + 2.11 \cdot x$ ($r = 0.92, p < 0.001$)	$y = -213 + 1.62 \cdot x$ ($r = 0.87, p < 0.001$)	$y = 65 + 1.40 \cdot x$ ($r = 0.88, p < 0.001$)
HCO ₃ ⁻ vs. *SO ₄ ²⁻	Black spring (N=22) $y = 270 + 0.86 \cdot x$ ($r = 0.68, p < 0.001$)	Dusan outflow (N=24) $y = 213 + 1.30 \cdot x$ ($r = 0.87, p < 0.001$)	Kvisla main (N=34) $y = 280 + 1.13 \cdot x$ ($r = 0.92, p < 0.001$)
*Ca ²⁺ + *Mg ²⁺ vs. SO ₄ ²⁻	$y = 257 + 1.36 \cdot x$ ($r = 0.75, p < 0.001$)	$y = 181 + 1.96 \cdot x$ ($r = 0.89, p < 0.001$)	$y = 208 + 2.27 \cdot x$ ($r = 0.95, p < 0.001$)
*Ca ²⁺ + *Mg ²⁺ vs. HCO ₃ ⁻	$y = 15 + 1.10 \cdot x$ ($r = 0.76, p < 0.001$)	$y = -83 + 1.37 \cdot x$ ($r = 0.93, p < 0.001$)	$y = 290 + 1.89 \cdot x$ ($r = 0.98, p < 0.001$)

Figures captions

Fig. 1. Location of study sites in the Werenskioldbreen basin in 2011, modified from an orthophoto map from 2011 (Norsk Polar Institute, <http://toposvalbard.npolar.no/>): 1 – Kvisla, 2 – Dusan outflow, 3 – Black spring, 4 – hydrometric station. Black triangles show supraglacial high streams flowing into the moulins.

Fig. 2. Seasonal variations in water chemistry, discharge and ablation rate in the Werenskioldbreen basin: A) concentrations of HCO_3^- , SO_4^{2-} and Ca^{2+} ; B) concentrations of Na^+ , Cl^- , K^+ and Mg^{2+} ; C) discharge at the hydrometric station, precipitation in Hornsund (Bania and Wawrzyniak, 2011a, b, c, d, e; Majchrowska and Małarzewski, 2011) and the ablation rate on Werenskioldbreen.

Fig. 3. The Piper diagram for water chemistry in the Werenskioldbreen basin.

Fig. 4. Concentrations of A) Na^+ and B) Cl^- vs. discharge during the entire ablation season at the hydrometric station in the Werenskioldbreen basin. Dotted circle shows the increase of concentration of Na^+ and Cl^- caused by the snowmelt.

Fig. 5. Dissolved constituents vs. discharge during the entire ablation season at hydrometric station in the Werenskioldbreen basin: A) Ca^{2+} ; B) Mg^{2+} ; C) Sulfate mass fraction (SMF).

Fig. 6. Ion associations at hydrometric station during three periods of the ablation season: early ablation (12 May - 18 June 2011), peak flow (19 June -10 September 2011) and late ablation (11 September -25 September 2011), and in the subglacial outflows of Black spring, Kvisla and New: A) $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. SO_4^{2-} , B) HCO_3^- vs. SO_4^{2-} , C) $\text{Ca}^{2+} + \text{Mg}^{2+}$ vs. HCO_3^- .

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6