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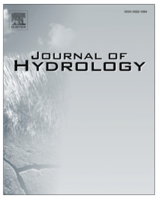

Chemical denudation and the role of sulfide oxidation at Werenskioldbreen, Svalbard

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SUMMARY

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

1. Introduction

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

Reactions that donate H^+ from the dissociation of organic and inorganic acids are particularly crucial for chemical weathering processes in these and other systems (e.g. Appelo and Postma, 2005), and in glacierized basins, H^+ ions are primarily derived from the dissociation of inorganic acids such as sulfuric, carbonic or nitric acids (Tranter et al., 1993) or simple hydrolysis (dissociation of H^+ from water, Tranter et al., 2002; Yde et al., 2005). While simple hydrolysis only dominates during the early phase of contact between water and minerals (Tranter and Wadham, 2013), sulfide oxidation and carbonation dominate in later phases and are the two main acid forming reactions which often are responsible for chemical weathering in glacierized catchments (Brown, 2002; Tranter et al., 2002). Sulfide oxidation in particular, which is usually coupled to the dissolution of carbonates and silicates, is

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potentially important in supporting primary productivity in oceans due to the delivery of iron (oxyhydr)oxide to ocean waters (Raiswell et al., 2006; Hawkings et al., 2014). Based on $^{34}S\text{-}SO_4^{2-}$ isotope concentrations (Wadham et al., 2004) and slope coefficients in regression equations (Tranter et al., 2002) and geochemical modelling (Mitchell and Brown, 2008), sulfide oxidation is a dominant geochemical control in many glacierized basins consisting of various rock types. For example, pyrite and Fe-bearing oxides in bedrock may fertilize subglacial biogeochemical processes (Mitchell et al., 2013), while the bulk mineralogy of bedrock appears to play a second-order effect on chemical weathering in glacierized catchments (Wadham et al., 2010b).

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

In basins with valley-type glaciers, chemical weathering is mainly influenced by bulk meltwater production and seasonal evolution of the subglacial drainage system. During the early ablation season, differential leaching of snowpack-derived solutes (mainly Na^+, Cl^-) dominates the chemical composition of the bulk meltwater and the contribution of solute from geochemical weathering processes is low (Wadham et al., 2000; Yde et al., 2008; Stachnik and Uzarowicz, 2011; Stachnik et al., 2014). At this time of year, subglacial conduits may be blocked by ice or snow dams, preventing them from draining the glacier efficiently (Irvine-Fynn et al., 2011). The breaking of these dams in combination with increased surface ablation causes the occurrence of an early discharge peak during the early ablation season (Brown, 2002). As the ablation season progresses a more effective channelized drainage system is 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, 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., 2001a) and to an enhancement of chemical weathering of silicates (Anderson, 2006; Mavris et al., 2012; Vilmundardóttir et al., 2014). Previous studies have shown that glacier forelands may account for 3–4 times more chemical denudation than the glacierized parts of basins (Anderson et al., 2000; Wadham et al., 2001a).

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, 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 CO_2 sequestration occurs in open channels (Hodson et al., 2002). Sulfate reduction is recognized 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, CO_2 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., 2001a).

This study focuses on the characteristics and differences between chemical processes in subglacial and proglacial zones of the glacierized basin of Werenskioldbreen on 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 glacierized 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 glacierized basin.

2. Study area

Werenskioldbreen (77°05′N, 15°15′E) is located in Wedel-Jarlsberg Land, Southwest Spitsbergen (Fig. 1). Its basin area covers 44.1 km^2, of which 27.4 km^2 are glacierized. The glacier is 9.5 km in length and is a typical land-terminating, valley-type polythermal glacier of this region of Svalbard (Hagen et al., 1993). The glacier elevation ranges from 60 to 650 m a.s.l. (Hagen et al., 1993) and the equilibrium line altitude (ELA) of the glacier is situated at ~450 m a.s.l. (Grabiec et al., 2012), although in the period 2009–2011 the ELA was above the maximal altitude of glacier (Ignatiuk and Migała, 2013). The mean annual mass balance was −0.43 m water equivalents during the period 1912–2005 (Grabiec et al., 2012). The maximum glacier thickness is approximately 235 ± 15 m (Ignatiuk and Migała, 2013), consisting of a 50–100 m thick surface layer of cold ice with temperate ice below (Pälli et al., 2003). At the ~50 m thick snout, the glacier is frozen to