Solute sources and geochemical processes in Subglacial Lake Whillans, West Antarctica

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ABSTRACT
Subglacial Lake Whillans (SLW), West Antarctica, is an active component of the subglacial hydrological network located beneath 800 m of ice. The fill and drain behavior of SLW leads to long (years to decades) water residence times relative to those in mountain glacier systems. Here, we present the aqueous geochemistry of the SLW water column and pore waters from a 38-cm-long sediment core. Stable isotopes indicate that the water is primarily sourced from basal-ice melt with a minor contribution from seawater that reaches a maximum of ~6% in pore water at the bottom of the sediment core. Silicate weathering products dominate the crustal (non-seawater) component of lake- and pore-water solutes, and there is evidence for cation exchange processes within the clay-rich lake sediments. The crustal solute component ranges from 6 meq L⁻¹ in lake waters to 17 meq L⁻¹ in the deepest pore waters. The pore-water profiles of the major dissolved ions indicate a more concentrated solute source at depth (>38 cm). The combination of significant seawater and crustal components to SLW lake and sediment pore waters in concert with ion exchange processes result in a weathering regime that contrasts with other subglacial systems. The results also indicate cycling of marine water sourced from the sediments back to the ocean during lake drainage events.

INTRODUCTION
Research over the past two decades has demonstrated abundant underwater basin beneath the Antarctic ice sheets, with subglacial water volume estimates of 10⁷–10⁸ km³ (Priscu et al., 2008). Water-rock interactions in glaciated catchments provide abundant reaction sites for chemical and biological weathering, which generates dissolved aqueous species (Tranter, 2004). Water beneath the West Antarctic Ice Sheet (WAIS) resides and flows in hydrologic networks of streams, lakes, and saturated sediment, leading to prolonged water-rock interactions and solute generation, with the waters ultimately draining to the ocean (Fricker et al., 2007; Skidmore et al., 2010; Carter and Fricker, 2012). These subglacial aqueous environments represent a source of suspended and dissolved biotic and abiotic components and fresh water to the Southern Ocean with potential impacts on ocean productivity, geochemistry, and circulation (Priscu et al., 2008; Statham et al., 2008).

Active subglacial lakes, such as those along the Siple Coast of West Antarctica, are an important component of the subglacial hydrologic system because they form reservoirs along the hydraulic drainage path to the Ross Sea. Subglacial Lake Whillans (SLW) and other lakes in the Siple Coast region are characterized as “active lakes” (Smith et al., 2009). The filling phase of the lake hydrological cycle occurs over ~2–4 yr, slowly increasing the depth and volume of the lake (Siegfried et al., 2014). Drainage events punctuate the filling cycle, moving large (~0.15 km³, in the case of SLW) volumes of water to the grounded margin of the Whillans Ice Stream and the Ross Sea (Carter and Fricker, 2012) on sub-decadal time frames. However, sediment-water interaction times beneath the Whillans Ice Stream can be thousands of years (Christoffersen et al., 2014). This contrasts with the hydrologic conditions beneath valley glaciers and marginal regions of the Greenland Ice Sheet where chemical weathering processes have been more widely studied (Tranter et al., 2002; Tranter, 2004; Wadhams et al., 2010). In these (non-Antarctic) subglacial systems, the main water source is surficial meltwater, and subglacial water-rock-contact times are typically much shorter, hours to months (Skidmore and Sharp, 1999; Tranter et al., 2002; Wadhams et al., 2010). Another important distinction between the non-Antarctic subglacial systems and SLW is that during interglacial periods, portions of the WAIS basin, including the present-day location of SLW, were periodically inundated by ocean water, and marine sediments accumulated (Scherer et al., 1998; Studinger et al., 2001). There may be a biogeochemical legacy from these deeper marine sediments that has yet to be explored, given the potential for chemical and redox gradients to exist, for example, with more anoxic and solute-rich sediment pore waters at depth, underlying shallow waters that are more dilute and oxic. Here we present the first detailed description of solute sources and geochemical processes for the water column and sediment pore waters from an Antarctic subglacial lake.

METHODS
Samples of water and sediment were collected from SLW (84.240°S, 153.694°W), 801 m beneath the WAIS, which was accessed using a clean, hot-water drill (Priscu et al., 2013). Water samples were collected from the middle of the ~2.2 m water column of SLW using a 10 L Niskin sampling bottle, and a 38 cm sediment core was retrieved with a multicorer (60 cm long × 6 cm diameter). Lake water samples for dissolved major ions and trace elements were filtered through 0.4 µm polycarbonate filters and 0.2 µm PTFE (polytetrafluoroethylene) filters, respectively. Samples of sediment pore water were extracted at 2 cm intervals using Rhizons (www.rhizosphere.com/rhizons) equipped with 0.2 µm pore-size filters, and distributed into cleaned vials. Samples for major ion and trace metal determinations were stored frozen before analysis via ion chromatography and inductively coupled plasma–sector field mass spectrometry (ICP-SFMS), respectively (Turetta et al., 2004; Montross et al., 2013). Stable isotopes (H and O) of the water were measured on unfrozen samples via cavity ring-down spectrometry. Silicon was determined colorimetrically (Iler, 1979). See the
RESULTS AND DISCUSSION

SLW Seawater Component

The lake water had a δ18O (H2O) value of −38.0‰ (Christner et al., 2014) with pore-water values increasing down core to −36.5‰ at 37 cm depth, the core bottom (Fig. 1A). δD (H2O) values showed a similar trend toward more positive values at depth (Fig. 1A). Lake water δD (H2O) values were comparable to those of meteoric ice from other Antarctic outlet glaciers (Souchez et al., 2004). A two-component mixing model of δ18O (H2O) was used to determine the percentage of glacial melt water and seawater in the SLW lake and pore waters (Phillips and Gregg, 2001), with δ18O (H2O) of −39‰, measured from deep glacial ice upstream of SLW (Vogel, 2004), as the glacial ice end member and 0‰ as the seawater end member. This analysis indicated that the lake water was composed of 97.4% glacial melt and 2.6% seawater, with the proportion of seawater increasing down core to a maximum of 6.4% at the core bottom, and the balance, 93.6% from glacial melt. Chloride concentrations also increased down core from 3.5 meq L–1 in the lake to 22.5 meq L–1 at the core bottom, equivalent to 4.1% of seawater Cl– concentration (Fig. 1B). The Cl– concentration profile is consistent with the stable isotope data indicating that the pore waters and solutes are partially derived from seawater. Chloride is a conservative tracer, and the linearity of the pore-water Cl– profile suggests that this system is in steady state, relative to the upward diffusion of Cl– from a more concentrated source at depth (>38 cm). The seawater influence is unlikely to be contemporary, as tidally driven pumping of modern, ice-shelf cavity seawater is limited to a distance of ~10 km upstream from the grounding line (Walker et al., 2013), whereas SLW is ~100 km upstream. The seawater signal measured at SLW is likely due to the lasting influence of past seawater inundation and deposition of marine sediments. The other major ions (Na+, K+, Mg2+, Ca2+, SO42–, and HCO3–) also show trends similar to that of Cl– with increased concentrations at depth and profiles that indicate upward diffusion from a more concentrated source (>38 cm depth) (Fig. 1B; Table DR1 in the Data Repository).

The Br–:Cl– in the lake waters was close to that of seawater, and we assumed all Cl– came from a seawater source (Christner et al., 2014). The seawater component of the pore waters was calculated using the Cl– concentration and the ratio of each ion to Cl– in seawater (Holmeck, 1987). The concentrations for Mg2+ are negative after applying the seawater correction, indicating a Mg2+ sink from solution exists in the sediment. Cation exchange reactions on clay minerals are the most likely sink given the high proportion (50% by dry weight; Table DR3) of silt- and clay-sized particles in SLW sediments, which is similar to the till composition found upstream of SLW (Tulaczyk et al., 1998).

SLW Solute from Crustal Weathering

We define whole water as the total solute load measured in the sample. The crustally derived, non-seawater component is defined as the total solute load with the seawater component subtracted. Following subtraction of the seawater component, significant crustally derived K+ and Na+ were evident in the SLW lake water and throughout the pore-water profile, likely from silicate mineral weathering (Fig. 1C), when compared to other subglacial waters (Fig. 2A). This is consistent with the mineralogical data on the sediments; e.g., the 63–125 μm size fraction was primarily composed of feldspar (35% of grains analyzed; n = 206; Table DR2). Aqueous Ca2+ and Mg2+ are typically sourced mainly from silicate or carbonate weathering, with a greater proportion of Ca2+ from carbonates than for Mg2+ (Meybeck, 1987). The concentrations for Mg2+ are negative after applying the seawater correction, indicating a Mg2+ sink from solution exists in the sediment. Cation exchange reactions on clay minerals are the most likely sink given the high proportion (50% by dry weight; Table DR3) of silt- and clay-sized particles in SLW sediments, which is similar to the till composition found upstream of SLW (Tulaczyk et al., 1998).

Clay minerals are prevalent in SLW sediments and provide cation exchange reaction sites that can modify Na+, K+, Mg2+, and Ca2+ ion concentrations derived from mineral dissolution and seawater sources. Ion exchange experiments on SLW sediments using a NaCl exchange solution with a similar concentration (20 meq L–1) to that at the bottom of the sediment core resulted in 0.9 meq g–1 Ca2+ and 0.6 meq g–1 Mg2+ desorbing from clay minerals. The exchange experiments demonstrate that clay minerals are a sink for Ca2+ and Mg2+ from SLW pore waters.

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1GSA Data Repository item 2016110, supplemental methods, geochemical data used for Figures 1 and 2 (Table DR1), Subglacial Lake Whillans sediment properties, grain composition (Table DR2), grain size distribution (Table DR3), and pyrite images (Figure DR1), is available online at www.geosociety.org/pubs/ft2016.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.
Weathering Regime in Subglacial Lake Whillans

Calcium is the dominant cation in alpine subglacial waters irrespective of lithology due to the rapid dissolution kinetics of carbonates (Anderson et al., 1997). By contrast, crustally derived Ca2+ is not a dominant ion in SLW, as demonstrated by the low Ca2+:Σcation molar ratio (0.04–0.13) compared to the world mean for glacial and non-glacial catchments (~0.45; Anderson et al., 1997). Na+ is the dominant crustally derived cation in SLW lake and pore waters. This is also true for samples from Antarctic subglacial waters beneath the Kamb Ice Stream, Bindschadler Ice Stream, and Casey Station which also have low crustally derived Ca2+:Σcation ratios: 0.22, 0.17, and 0.09, respectively (Skidmore et al., 2010). The low Ca2+:Σcation ratios from Antarctic subglacial aqueous samples are generated through a different weathering regime from Ca2+-dominated Alpine glacial systems. These lower Ca2+:Σcation ratios are most likely due to increased silicate weathering and ion exchange reactions during longer water-rock interaction times in Antarctic subglacial environments. Long water residence time produces proportionately greater amounts of crustally sourced Na+ and K+ to the subglacial waters (Wadham et al., 2010). Clay minerals in SLW sediments are also a product of long-term silicate weathering and are not observed in valley glacier tills characterized by shorter residence times (e.g., Griggs, 2013). The Mg2+ and Ca2+ concentrations in SLW waters are lower than one would expect from such long residence-time waters, and the deficit is assumed to be due to cation exchange on clay minerals, leading in part to the low Ca2+:Σcation ratio.

Silicate weathering can occur abiotically, but given the presence of an active microbial community in SLW (Christner et al., 2014) and previous research demonstrating the key role of microbes in weathering of glacial sediments (Montross et al., 2013), biotic weathering may also occur. CO2 released from heterotrophic activity in the SLW water column (Christner et al., 2014) will dissolve and produce carbonic acid, which is responsible for indirect weathering of minerals (Montross et al., 2013) and contributes in part to the HCO3- in the lake and sediment pore waters. The balance of HCO3- may come from carbonate dissolution and possibly hydrothermal sources given the high geothermal heat flux in the region (Fisher et al., 2015). Direct weathering of sulfur-containing minerals (i.e., pyrite), which are present in SLW sediments (Fig. DR1 in the Data Repository), through sulfide oxidation produces protons and dissolved SO42- (Fig. 1B). Microbial sulfide oxidation is inferred from the excess of crustally derived SO42- with respect to Cl- in the top 15 cm of the core (Fig. 1D) and has been demonstrated in other glacial sediments (Mitchell et al., 2013; Boyd et al., 2014). Microbial community and functional gene analysis of SLW and Kamb Ice Stream sediment supports the possibility of microbial pyrite oxidation, as microbial phenotypes and sulfide-oxidizing functional genes related to sulfide-oxidizing bacteria are present and abundant in these environments (Lanoil et al., 2009; Christner et al., 2014; Purcell et al., 2014). These microbially driven sulfide oxidizing processes are likely the source of crustally derived, non-seawater sulfate in SLW.

Microbial sulfide oxidation is most energetically favorable in the presence of O2. To estimate the depth below which sulfide oxidation is unlikely to occur, we estimated the reduction-oxidation (redox) state of the sediment using the charge of the element vanadium (V) and thus its aqueous concentration. Redox-sensitive elements, such as V, are useful indicators of the redox state of the sediments (Morford and Emerson, 1999). As dissolved O2 concentrations decrease, vanadate (H2VO4–) is reduced to vanadyl [V(IV)O2+], and V is removed via precipitation (Morford and Emerson, 1999). Therefore, the decrease in V concentrations to below detection at depths lower than 15 cm in the SLW sediments implies decreasing O2 concentrations with depth (Fig. 1E). The O2-consuming processes are likely microbial, involving either heterotrophic or lithotrophic activity such as sulfide and ammonia oxidation, processes which are thought to be important in SLW (Christner et al., 2014). The silicon profile is similar to that of V and shows that silicon concentrations are highest in the surficial (0–2 cm) sediments (Fig. 1E). Increased microbial activity in the surficial sediments may be due to the presence of oxidizing conditions, unlike those at depth. Microbial activity in the sediments is therefore likely to be important in liberating solutes via both direct and indirect biotic weathering processes.

CONCLUSIONS

Crustally derived solute in SLW is generated primarily from the weathering of silicate minerals, a process that is likely microbiologically mediated. Ion exchange reactions with clay minerals also modify the proportions of cations in solution. Seawater is also an important component of SLW solute, in contrast to Kamb Ice Stream and Bindschadler Ice Stream pore waters and subglacial waters from other non-Antarctic systems. The major ion profiles all indicate a more concentrated solute source in pore water of sediments below the base of our 38 cm core, which we were unable to sample. These deeper pore waters likely have an increased seawater component, resulting from marine inundation of the SLW region when the WAIS was less extensive. SLW represents a subglacial system where
contemporary chemical and biological weathering processes are active but seawater solute is a component of the water that is ultimately cycled back to the Southern Ocean during lake drainage.

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