Chemical Weathering Trends in Fine-Grained Ephemeral Stream Sediments of the McMurdo Dry Valleys, Antarctica

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Abstract

We investigated chemical weathering trends within the fine-grained (<63 μm ; silt and clay) fraction of sediments collected from meltwater streams emanating from glaciers in the McMurdo Dry Valleys (MDV; Wright and Taylor Valleys) by integrating grain size, BET surface area, and whole-rock geochemistry. While both valleys currently host cold-based glaciers, the sediment underlying the ephemeral glacial streams was deposited under differing glacial conditions. In Wright Valley (Clark Glacier stream), Brownworth and Trilogy drifts were deposited via cold-based glaciation, whereas the Ross Sea drift that underlies Delta Stream in Taylor Valley likely reflects contributions from wet-based ice. Wright Valley stream sediments are typically coarser grained and have a higher silt content as compared to Taylor Valley sediments. These sediments consist primarily of pyroxenes, quartz, and feldspars, with the

percentages of pyroxenes and quartz systematically increasing downstream. The percentage of phyllosilicates ranges from 4-18% and decreases with downstream distance. In contrast, Taylor Valley sediments (Delta Stream) are finer-grained and exhibit lower percentages of both pyroxene and quartz and a significantly higher percentage of phyllosilicates (30-43%).

Concentrations of all mineral phases remain relatively consistent in abundance with downstream transport in the Delta Stream transect as compared to Clark Glacier stream sediments. Standard chemical weathering indices, such as the Chemical Index of Alteration (CIA), indicate that chemical weathering is occurring within the silt and clay fractions of Antarctic stream sediments and is particularly pronounced in Delta Stream sediments that have BET surface area measurements $>40 \text{ m}^2/\text{g}$. Utilization of MFW (mafic-felsic-weathered) and A-CN-K ($\text{Al}_2\text{O}_3\text{-CaO} + \text{Na}_2\text{O-K}_2\text{O}$) plots, however, are more effective in discerning the extent and nature of chemical weathering in these stream systems. Ca and Na depletion observed within the sediments exhibiting the highest surface area in Delta Stream suggest that chemical weathering may result in pitting and/or incongruent dissolution of pyroxenes and feldspars, as well as the development of amorphous and/or nanophase weathering products. In contrast, Clark Glacier stream sediments do not have similar leaching trends in the fine-grained sediment fraction and exhibit minimal weathering overall. This may suggest that fine-grained material is being trapped on top of the Clark Glacier surface and has not yet been transported into the weathering environment of the hyporheic zone due to timing of sampling. Alternatively, complete dissolution of very fine-grained sediment could be occurring in this stream transect, and is therefore not preserved in the fine sediment fraction. Overall, the magnitude of chemical weathering observed between the two stream systems is ultimately related to the nature of the underlying drift (cold and wet-based drift

deposition), dispersal patterns of eolian fines, and variable stream discharge rates. Thus, incorporation of local fine-grained sediment derived from the underlying glacial drift deposits and distributed via the varying wind regimes within the hyper-arid climate into active stream channels may facilitate incongruent mineral dissolution and development of weathering products, and ultimately influence the composition and concentration of meltwater stream solutes.

1. Introduction

Weathering in polar climates is considered to be dominated by physical processes, including rock fragmentation due to thermal processes, and wind abrasion that produces ventifacts (Hall et al., 2002; Huh, 2003; Sepala, 2004; Putkonen et al., 2014). Chemical weathering in cold regions has been previously assumed as minimal owing to limited availability of liquid water, and low temperatures that slow reaction rates (Velbel, 1993; Lasaga et al., 1994; White and Blum, 1995; Anderson et al., 1997; Anderson, 2007; Hall et al., 2002; Goudie and Viles, 2012). However, in wet-based glacial regimes, mechanical grinding of sediments by glacial erosion can produce large volumes of unsorted sediment including fresh rock flour with high surface area susceptible to significant chemical weathering attributable to formation of chemically reactive sites on mineral grains (Anbeek 1992, 1993; Anderson, 2005, 2007; Goudie and Viles, 2012). Chemical erosion rates in glacial systems are typically correlated with water discharge rates, and cation fluxes in these systems commonly reflect ready dissolution of soluble carbonate phases and leaching from abraded silicate minerals such as biotite (Anderson et al., 1997; Nezat et al., 2001). However, a recent long-term meltwater chemistry study within the

temperate proglacial system of Austre Broggerbreen (Norway) (Nowak and Hodson, 2014) revealed enhanced silicate mineral weathering owing to exposure of fine-grained, chemically reactive sediments during glacial retreat associated with a transition from wet-based to cold-based conditions and decreased discharge. These results suggest that exposed mineral surface area may be even more important than water flux in controlling ion yields in wet-based glacial systems.

In the McMurdo Dry Valleys of Antarctica, cold-based glaciers currently dominate across the landscape. These valleys were subject to wet-based glaciation during the Oligocene, followed by development of cold-based glaciation during the Miocene (~13.6 Ma). The MDV have maintained cold, hyper-arid conditions since this time (Marchant et al., 1993; Denton and Sugden, 2005; Sugden et al., 2006; Bockheim, 2013). Cold-based glaciers are defined as those frozen to the rock substrate, suggesting minimal erosive impact on subjacent bedrock and sediment. However, some active basal sliding has been documented in the MDV, resulting in geomorphic features such as boulder-top abrasion, grooves, and thin drift deposits (Chinn, 1994; Cuffey et al., 2000; Atkins et al., 2002; Atkins, 2014). The various drift deposits that currently fill the MDV, however, reflect complex and differing glacial histories, and include derivation from both wet-based and/or cold-based glaciation.

Previous work on the magnitude and nature of chemical weathering in Antarctic streams has focused on assessing variations in solute concentrations within stream waters sourced from cold-based glaciers and their transport into ice-covered lakes (Green et al., 1988; Lyons et al., 1998; Nezat et al., 2001; Gooseff et al., 2002; Lyons et al., 2002; Lyons et al., 2003; Gooseff et

al., 2004; Green et al., 2005; Fortner et al., 2005; Welch et al., 2010; Stumpf et al., 2012; Fortner et al., 2013). These solutes are attributed to dissolution of salts and carbonates and weathering of silicate minerals within channel and hyporheic soil sediments (Lyons et al., 1998; Gooseff et al., 2002; Stumpf et al., 2012). Based on observed solute trends, chemical weathering in MDV streams can occur at rates per unit area equivalent to wet-based glacial systems, despite prevailing low temperatures, seasonally restricted moisture availability, and minimal organic content (Nezat et al., 2001; Lyons et al., 2002; Gooseff et al., 2002; Welch et al., 2010; Stumpf et al., 2012). However, due to the complex history of the glacially derived till, these rates may reflect a relict of a former wet-based setting.

Despite well-documented observations of heightened solute loads in ephemeral Antarctic glacial streams, few studies directly assess the impact of silicate weathering on sediments within the stream hyporheic zone and/or identify potential weathering products (i.e., clays) (Lyons et al., 1998; Gooseff et al., 2002; Maurice et al., 2002). Here, we present geochemical data on fine-grained ($<63\ \mu\text{m}$) hyporheic zone sediments from stream channels in both Wright and Taylor Valleys (Antarctica) to investigate the characteristics and potential variability of chemical weathering in ephemeral proglacial stream sediments within a modern cold-based glacial environment. In addition, we explore potential links among past glacial conditions (i.e., wet versus cold-based glaciation), eolian contributions, stream discharge, and supraglacial processes.

2. Geologic Setting

The MDVs are a series of east-west trending, nearly ice-free valleys situated between the Transantarctic Mountains and the Ross Sea of Antarctica. The MDV region is classified as a

hyper-arid, polar desert where mean annual temperatures range between -14.8 °C and -30.0 °C, and precipitation, typically in the form of snowfall, is <10 cm/yr (Clow et al., 1988; Fountain et al., 1999; Doran et al., 2002; Doran et al., 2008). The hydrologic elements of the MDV consist of glaciers, ephemeral streams, lakes, and shallow groundwater. Continuous permafrost occurs at shallow depths throughout the MDV, spatially restricting subsurface flow (Gooseff et al., 2011). Active stream flow is limited to the austral summer (approximately 6-12 weeks), when solar insolation warms the surfaces of valley glaciers and generates meltwater runoff, which flows off the glaciers and across valley drift to closed-basin lakes. Streamflow rates exhibit diel variation, and can fluctuate 5-10 fold within a single summer day (McKnight et al., 1999; Gooseff et al., 2011; McKnight, 2014). Meltwater exchange with drift sediments primarily occurs within the hyporheic zone of reactivated stream channels, defined as the saturated area underlying and adjacent to the streambed where water can flow before encountering permafrost (McKnight et al., 1999; Gooseff et al., 2002; Gooseff et al., 2013).

Additional shallow groundwater features include melt from localized snow patches, water tracks, and margins of streams and lakes, which, in conjunction with the hyporheic zone, mobilize solutes and provide suitable conditions for biotic growth and biogeochemical cycling (Barrett et al., 2009; Levy et al., 2011; Gooseff et al., 2013; Langford et al., 2014; Mikucki et al., 2015). Biotas in the MDV are generally restricted to cyanobacteria, algae, and mosses. Perennial algae typically grow within streams as mats that can endure long periods of desiccation and are common within Taylor Valley streams (McKnight et al., 1999; McKnight et al., 2007).

Eolian processes in the MDV are critical to distributing nutrients, organic matter, and sediment onto glacier surfaces and into the hyporheic zones of the ephemeral stream channels, where these particulates may become entrained in meltwater runoff and into stream flow (Fortner et al., 2011; Sabacka et al., 2012; Deuerling et al., 2014). Winds blow up-valley from McMurdo Sound during the summer months, whereas strong down-valley winds sourced from the polar plateau prevail during the winter and can reach speeds up to 40 m/s (Doran et al., 2008). Summer foehn wind events can also result in adiabatic warming of the MDV region, leading to heightened temperatures and increased meltwater generation (Steinhoff et al., 2014). Wind-blown aerosols are typically either marine or locally sourced terrestrial material, and particulate concentrations are commonly higher on the western sides of glaciers due to the prevailing wind direction (Lyons et al., 2003; Bertler et al., 2004; Ayling and McGowan, 2006; Witherow et al., 2006; Williamson et al., 2007; Sabacka et al., 2012; Fortner et al., 2013; Duerling et al., 2014).

This study focuses specifically on sample sites in eastern Wright (Clark Glacier stream) and eastern Taylor (Delta Stream and Goldman Glacier channel) Valleys (Fig. 1). Whereas granitic plutonic and metamorphic rocks underlie both field areas, the overlying drift deposits reflect differing glacial histories and contain materials of differing composition, texture, and age. In lower Wright Valley, drift deposits are underlain by the Brownworth (granite and quartz monzonite) and Denton (foliated granodiorite) plutons near the eastern end of the valley and adjacent to Wright Lower Glacier. Drift types in this region date to at least the Miocene and were largely emplaced prior to the Last Glacial Maximum (LGM). These drift deposits generally consist of a coarse-grained, heterogeneous mix of igneous and metamorphic clasts and were sourced from multiple cold-based glacial ice advances and retreats from the adjacent Wilson

Piedmont Glacier and Ross Sea Embayment (Hall and Denton, 2005). The stream emanating from Clark Glacier (henceforth referred to as Clark Glacier stream) in Wright Valley crosses Brownworth drift, which is underlain by Trilogy drift near the glacier terminus and Loke drift near Lake Brownworth (Fig. 1). Brownworth drift is dominated by sand-size material and consists of two facies: 1) coarse sand diamicton, and 2) horizontally stratified sandy glaciolacustrine facies. The drift exhibits limited soil development and consists of a variety of basement clast types, including Ferrar dolerite, Olympus granite gneiss, Vida granite, and microdiorite (Hall and Denton, 2005).

Fig. 1. (a) Location map of sampling sites for this study in Wright Valley. “CG” refers to samples collected from the meltwater stream emanating from Clark Glacier. “Brown drift” refers to the representative sample collected from Brownworth drift. The underlying bedrock for the Clark Glacier stream is the Brownworth Pluton. Shaded polygons represent the mapped drift deposits (Hall and Denton, 2005) in the vicinity of Clark Glacier stream, which is directly underlain by Brownworth drift. (b) Location map of sampling sites for this study in Taylor Valley. “DS 2-13” refers to samples collected from the meltwater stream emanating from Howard Glacier (formally named Delta Stream) during the 2009-2010 field season. “DS a, b, c” refers to samples collected from Delta Stream during the 2012-2013 field season. These samples are underlain by bedrock

composed of biotite orthogneiss and directly by Ross Sea drift (Hall et al., 2000). “Gold” refers to samples collected from the channel transect emanating from Goldman Glacier, which are underlain by undifferentiated pre-Bonney drift (Hall et al., 2000). No stream flow was observed in the Goldman Glacier stream transect during sampling for this study.

Eastern Taylor Valley is primarily underlain by biotite orthogneiss and filled by undifferentiated and Ross Sea drift sediments. The stream emanating from Howard Glacier (formally named Delta Stream) crosses Ross Sea drift exclusively, which was emplaced during the LGM and reflects deposition by partially wet-based ice that encroached from the Ross Sea (Hall et al., 2000). Ross Sea drift, therefore, contains sediments derived from both wet and cold-based deposition, with marine input. The drift consists of five distinct facies (till, waterlain diamicton, glaciolacustrine silt, stratified sand, and stratified silt-sand-gravel), is notably finer grained compared to Wright Valley drift deposits, and, in addition to granite and metamorphic basement clasts, has a distinct lithology of kenyte, basalt, sandstone, and dolerite erratics from sources beyond eastern Taylor Valley (Hall et al., 2000). The Goldman Glacier stream channel flows over undifferentiated pre-Bonney drift, which has not been extensively described in the literature (Hall et al., 2000).

3. Methods

Sediment samples (~500-1,000g/site) were collected from surficial deposits within Clark Glacier stream (originating from Clark Glacier in Wright Valley and terminating at the Onyx River) and Delta Stream (originating from Howard Glacier, Taylor Valley and terminating into Lake Fryxell) during the 2009-2010 austral summer field season (Fig. 1). Both stream channels

contained actively flowing water, and stream sediments were sampled at 400-500 m intervals within areas of active deposition (i.e., marginal bars) and flow of the stream channel. Sample collection occurred during a comparatively low-flow year, when seasonal average discharge for Delta Stream was 3.7 l/s (1.6 l/s on the day of sampling; McKnight, 2014). The average seasonal discharge for the previous (2008-2009) and subsequent (2010-2011) austral summers was 70.01 l/s and 51.4 l/s, respectively. No stream gauge data are available for Clark Glacier stream during our sampling season or recent years. However, observable flow within Clark Glacier stream was greater than in Delta Stream during sampling (January 9, 2010 and January 18, 2010, respectively). Two representative drift samples were collected near (within 2-210 m) each main flowing stream transect, and sediment samples were also collected from a stream channel emanating from Goldman Glacier in Taylor Valley, which was dry when sampled but has been seasonally wet in recent periods (Levy et al., 2011; Levy, 2012). Additional sediment samples along Delta Stream were collected during the 2012-2013 field season (average seasonal discharge of 6.5 l/s; McKnight, 2014) for temporal comparison. All sediments were kept frozen following field collection until they were processed for grain size, surface area, and geochemical analyses in laboratories at the University of Oklahoma.

Samples were processed as outlined in Marra et al. (2014, 2015). Briefly, sediments were wet sieved to split the gravel, sand, and mud (silt and clay; $<63\ \mu\text{m}$) fractions. As finer-grained material generally has higher sediment surface area, and is thus considered to be more chemically reactive by mass or volume, our analyses focus primarily on the silt and clay fraction ($<63\ \mu\text{m}$ grain size, referred to subsequently as mud). In order to analyze only the silicate mineralogy, the mud fraction was treated for 24 h with buffered acetic acid to remove carbonate

coatings on grains, and with hydrogen peroxide (30% grade for 30 min) to remove organic material. The mud samples were freeze-dried and analyzed for grain size to determine the relative percentages of silt and clay with a Beckman Coulter Laser Particle Size Analyzer (LPSA), and N₂ adsorption BET surface area (Brunauer et al., 1938) with a Beckman Coulter SA3100 analyzer (Marra et al., 2014, 2015).

A subset of the mud fraction was analyzed for whole-rock geochemistry utilizing lithium borate fusion and ICP-AES by a commercial laboratory (ALS Chemex). Whole-rock geochemical data were reported as weight percent oxides. In order to focus specifically on the silicate fraction, values of CaO were corrected to account for Ca bound in apatite according to the equation (Girty et al., 2013):

$$\text{CaO}^* = \text{CaO} - (3.33 * \text{P}_2\text{O}_5)$$

Bulk quantitative x-ray diffraction (XRD) analyses of the processed muds were run on a Rigaku Ultima IV at the University of Oklahoma. Oriented clay mounts of the <2 µm clay fraction were analyzed with a Siemens D-500 (fixed-slit assembly and Bragg-Brentano geometry) at the USGS in Denver, CO. XRD patterns were interpreted with JADE and ClaySim software packages (Appendix A).

4. Results and Discussion

4.1 Grain size

Within the mud (<63 µm) fraction of the analyzed sediments, relative concentrations of silt and clay-sized material vary considerably between the streams in Wright and Taylor valleys,

and fluctuate along sampled transects (Fig. 2). Wright Valley sediments are generally coarser, with silt composing 63-91% of the total mud fraction. Silt increases (and clay-sized sediment correspondingly decreases) down the Clark Glacier stream transect, with a significantly higher percentage of clay-sized material (~33%) noted in the Brownworth drift sample compared to all but one of the stream sediments (<20%, Marra et al., 2014, 2015). In Taylor Valley, the overall percentages of clay-sized sediment in the mud fraction are higher than in Wright Valley (Fig. 2b). Sediments from Delta Stream have the highest percentage of clay-sized material in the mud fraction (14-50%), whereas clay-sized percentages in the Goldman Glacier dry channel transect are slightly lower (14-29%; Fig. 2b), and drift sediments collected away from the stream channel have similar concentrations of clay-sized sediments.

The differences in clay and silt content may be attributable to differing origins of the underlying valley drift sediments (Hall and Denton, 2005; Marra et al., 2015). Brownworth drift (Wright Valley) was deposited via cold-based glaciation, which suggests that derivation of glacially ground fines would be minimal in this system and could explain the overall relative paucity of fine-grained material in this valley (Hall and Denton, 2005). In contrast, Ross Sea Drift (Taylor Valley) was deposited by partially wet-based ice advancing from the Ross Sea, which likely contained significant fine-grained, glacially ground sediment (rock flour) derived from East Antarctic tributaries (Hall et al., 2000). In addition, fine-grained marine sediments from the Ross Sea would have also been incorporated into deposits during wet-based ice incursion into Taylor Valley (Hall et al., 2000; Hall and Denton, 2005).

Fig. 2. (a) The total percentage of the mud fraction (< 63 μm) for each channel and drift sample as obtained by wet-sieving. Taylor Valley samples are generally finer-grained overall with a higher percentage of mud as compared to Wright Valley samples. (b) The percentage of silt and clay-sized material within the mud fraction as obtained by laser particle size analysis. Taylor

Valley samples have a higher percentage of clay-size material within the mud fraction as compared to Wright Valley samples.

4.2 Elemental abundances and XRD analyses

Whole-rock geochemical data for Antarctic drift and channel sediments analyzed in this study appear in Table 1. Carbonates and salts can be prevalent within MDV soils, related to the development of paleolakes and common pedogenic processes (Keys and Williams, 1981; Bockheim, 2013; Toner et al., 2013). In addition, the deposition of marine-sourced aerosol salts into the MDV region from the Ross Sea commonly occurs during varying wind regimes in the summer months (Bertler et al., 2004; Witherow et al., 2006; Williamson et al. 2007; Sabacka et al., 2012; Fortner et al., 2013). A corresponding study by Stumpf et al. (2012) addressed stream solute trends within the sampled transects discussed here. While Stumpf et al. (2012)

Sample ID	Distance (km)	Whole rock geochemistry (wt %)									
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	CaO*	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅
Wright Valley											
CG-1	0	54.0	15.4	7.8	4.4	6.6	5.5	2.8	2.1	1.3	0.3
CG-2	0.4	55.2	16.2	8.4	3.9	5.4	4.3	2.9	2.6	1.4	0.3
CG-3	0.8	52.8	14.9	8.5	4.4	5.9	4.8	2.6	2.2	1.5	0.3
CG-4	1.4	51.9	12.5	11.6	6.4	7.8	6.2	2.2	1.5	2.8	0.5
CG-5	1.8	54.1	14.8	8.8	5.1	7.1	5.8	2.6	2.0	1.6	0.4
CG-6	2.3	53.1	14.4	8.8	5.0	7.0	5.7	2.6	1.9	1.7	0.4
CG-7	3.3	51.8	12.9	9.7	5.7	7.5	6.0	2.3	1.6	1.9	0.5
CG-8	3.7	53.7	13.7	8.8	5.5	7.5	6.3	2.4	1.7	1.5	0.4
CG-9	4.2	53.7	13.6	10.0	5.7	7.5	6.2	2.4	1.7	2.0	0.4
CG-10	4.7	53.5	13.0	10.1	6.4	8.4	6.8	2.3	1.5	1.9	0.5

<i>CG Average</i>		<i>53.4</i>	<i>14.1</i>	<i>9.2</i>	<i>5.3</i>	<i>7.1</i>	<i>5.8</i>	<i>2.5</i>	<i>1.9</i>	<i>1.8</i>	<i>0.4</i>
Brownworth drift	0.2	58.0	15.4	7.0	4.1	6.8	6.1	2.7	2.3	0.9	0.2
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Taylor Valley											
DS-13	0.0	51.9	14.5	9.3	4.6	5.5	4.4	2.6	2.4	1.6	0.3
DS-12	0.1	51.7	14.0	9.9	4.0	3.7	2.9	2.0	2.7	1.7	0.3
DS-11	0.6	52.2	14.5	9.4	4.5	5.4	4.3	2.8	2.3	1.6	0.3
DS-10	1.0	49.2	14.7	11.4	4.4	2.9	2.0	1.7	3.0	1.8	0.3
DS-9	1.5	51.9	14.7	8.5	4.0	4.5	3.4	2.9	2.5	1.3	0.3
DS-8	1.9	47.9	13.8	10.1	4.0	3.2	2.1	1.8	2.7	1.6	0.4
DS-7	2.4	51.9	15.0	9.4	4.2	4.3	3.3	2.7	2.6	1.5	0.3
DS-6	2.9	52.2	14.0	9.8	4.2	3.8	2.8	1.9	2.6	1.6	0.3
DS-5	3.4	51.1	15.0	9.7	4.5	4.5	3.5	2.8	2.3	1.5	0.3
DS-4	3.9	53.9	12.8	8.9	4.2	4.2	3.4	1.9	2.2	1.5	0.2
DS-3	4.3	47.6	14.5	11.4	4.8	3.2	2.3	2.7	2.3	1.8	0.3
DS-2	4.8	53.3	14.1	9.8	4.0	3.7	2.7	1.8	2.5	1.8	0.3
<i>DS 2010 Average</i>		<i>51.2</i>	<i>14.3</i>	<i>9.8</i>	<i>4.3</i>	<i>4.1</i>	<i>3.1</i>	<i>2.3</i>	<i>2.5</i>	<i>1.6</i>	<i>0.3</i>
DS-c	1.9	51.0	14.6	10.3	4.6	4.0	2.9	2.3	2.6	1.6	0.3
DS-b	3.1	43.5	12.1	8.8	4.3	5.8	4.3	1.8	2.3	1.4	0.5
DS-a	3.9	47.7	12.9	9.9	4.9	5.8	4.3	2.3	2.2	1.5	0.4
<i>DS 2013 Average</i>		<i>47.4</i>	<i>13.2</i>	<i>9.6</i>	<i>4.6</i>	<i>5.2</i>	<i>3.9</i>	<i>2.1</i>	<i>2.4</i>	<i>1.5</i>	<i>0.4</i>
Ross Sea drift	0.002	55.8	13.5	8.8	5.5	6.4	5.2	2.3	2.1	1.4	0.4
Gold-1	0.0	47.7	15.4	11.4	5.3	4.8	3.6	2.2	2.5	1.8	0.4
Gold-5	0.5	50.2	14.3	10.0	5.1	5.6	4.2	2.2	2.3	1.6	0.4
Gold-8	1.3	54.1	13.7	9.1	5.7	7.0	5.6	2.3	1.9	1.5	0.4
<i>Gold Average</i>		<i>50.7</i>	<i>14.5</i>	<i>10.2</i>	<i>5.4</i>	<i>5.8</i>	<i>4.5</i>	<i>2.3</i>	<i>2.2</i>	<i>1.7</i>	<i>0.4</i>
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Wichita Mountains											
RBB 6	0	70.4	10.1	2.81	0.48	0.35	0.12	1.52	2.77	0.98	0.07
RBB 9	1.5	68.3	9.89	3.29	0.39	0.32	0.05	1.73	3.04	0.93	0.08
RBB 12	3	68.3	9.7	3.5	0.4	0.5	0.25	1.8	2.9	1.0	0.1
RBB 13	3.5	65.1	10.6	5.68	0.51	0.46	0.06	1.85	3.01	1.31	0.12

<i>Wichita Average</i>	<i>68.0</i>	<i>10.1</i>	<i>3.8</i>	<i>0.4</i>	<i>0.4</i>	<i>0.1</i>	<i>1.7</i>	<i>2.9</i>	<i>1.1</i>	<i>0.1</i>
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Table 1. Whole-rock geochemistry for sample sites in Wright and Taylor valleys, Antarctica.

Values are reported as weight percent oxides. Four samples collected within Blue Beaver Creek (RBB) in the Wichita Mountains, Oklahoma are included for comparison. CaO* refers to calcium corrected measurements based on the formula $\text{CaO}^* = \text{CaO} - (3.33 \cdot \text{P}_2\text{O}_5)$ to account for calcium bound in apatite (Girty et al., 2013). The analytical margin of error for samples analyzed by ALS-Chemex laboratories is +/- 5%.

demonstrated that solute trends are affected by dissolution of carbonates and salts in the bulk sediments, this study instead focuses on the silicate fraction of the stream sediments. Therefore, carbonates and salts were removed from the sediments via wet sieving and acetic acid treatment prior to geochemical analysis of the silt and clay fraction.

In Clark Glacier stream (Wright Valley), the overall elemental abundances in the mud-sized silicate fraction are: Si > Al > Fe > Ca Mg > Na > K (Table 1; Fig. 3). Bulk quantitative XRD analyses indicate that the mud-sized silicate fraction is composed predominantly of primary minerals (i.e., quartz, feldspars, and pyroxenes at a range of 81 to 96%), where the percentages of quartz and pyroxenes both systematically increase downstream and the percentage of feldspar decreases (Fig. 4). Among the feldspars, plagioclase > alkali feldspar, although the range of feldspar phases present was difficult to distinguish with the XRD data. The remaining mineral fraction (4-18%) is composed primarily of phyllosilicate phases, including biotite and chlorite, with minor illite, kaolinite, and smectite, which correspondingly decreases

downstream along the transect (Appendix A). Accordingly, concentrations of Ca, Mg, and Fe (likely associated with the high pyroxene content) increase downstream, whereas Na, K, and Al associated with feldspar and phyllosilicate phases (i.e., biotite and chlorite) decrease downstream (Fig. 3).

Fig. 3a-g. Whole-rock geochemistry (in weight percent) of mud samples along transect. Drift samples are plotted to the right in each graph for comparison. In Clark Glacier stream, concentrations of Al, Na, and K decrease whereas Mg and Ca increase with downstream distance. P-values for Al, Mg, Ca, Na, and K in relation to downstream distance are <0.05 for Clark Glacier stream. In Delta Stream, Ca, Na, and K show a slight decrease in abundance downstream, although both Ca and Na exhibit a fairly erratic pattern along the stream transect. However, none of the correlations for elemental abundances versus distance in Delta Stream are statistically significant at the 0.05 significance threshold.

Fig. 4. (a) Percentage of primary minerals along transect for Clark Glacier stream (diamonds) and Howard Glacier (Delta Stream, shown as squares) samples collected in 2010 as obtained via

bulk quantitative XRD analysis. All mineral phases identified by the XRD analyses are set to sum to 100%. The percentages of primary minerals increase downstream in Clark stream and are greater in abundance compared to Delta Stream. (b) Percentage of quartz in Clark Glacier stream and Delta Stream samples along transect. The percentage of quartz increases downstream Clark Glacier stream but remains uniform in abundance in Delta Stream. The p-value for quartz versus distance is <0.05 in Clark Glacier stream. (c) Percentage of feldspars (plagioclase and K-feldspar) in Clark Glacier stream and Delta Stream samples along transect. The total percentage of feldspars decreases slightly downstream in Clark Glacier stream and increases slightly in Delta Stream with downstream distance. The relative percentage of feldspars in both stream transects is approximately equal. (d) Percentage of pyroxenes in Clark Glacier stream and Delta Stream samples along transect. The percentage of pyroxenes notably increases in Clark Glacier stream transect with downstream distance and is greater in abundance compared to Delta Stream. The p-value for pyroxenes versus distance in Clark Glacier stream is <0.05 . The percentage of pyroxenes slightly decreases in Delta Stream downstream.

In Taylor Valley (Delta Stream and Goldman channel transect), the relative elemental abundances in the mud fraction are: $\text{Si} > \text{Al} > \text{Fe} > \text{Mg} > \text{Ca} > \text{Na} > \text{K}$ (Table 1; Fig. 3). XRD analyses of the mud fraction of Delta Stream sediments collected in 2010 show that the primary mineral fraction is approximately 57-70% of the samples, with feldspars $>$ pyroxene $>$ quartz (Fig. 4). Quartz remains relatively consistent in abundance downstream, whereas the percentage of feldspars increases and the percentage of pyroxenes decreases minimally along transect. Among the feldspars, potassium feldspars $>$ plagioclase feldspars, although individual feldspar phases were also difficult to distinguish with the XRD data in this stream system. The remaining

30-43% of the mineral fraction is composed of phyllosilicate phases (biotite, chlorite, illite, and mixed-layer clays, with minor kaolinite, smectite, and vermiculite; Appendix A).

Elemental abundances for Si, Al, Fe, Mg, and K remain relatively consistent within the mud fraction down the Delta Stream transect in accordance with the consistent downstream abundance of both primary and phyllosilicate minerals (Fig. 4). Only Ca, Na, and K exhibit a slight decrease in abundance downstream, although these are not robust trends ($p > 0.05$) and all elements exhibit a fairly erratic pattern along the stream transect (Fig. 3). Whole-rock geochemistry for additional Delta Stream samples collected in 2013 correlate well with the elemental abundances obtained for 2010 samples (Fig. 3). Mud within a drift sample (Ross Sea drift) collected adjacent to Delta Stream also exhibits a similar geochemical signature to mud collected within Delta Stream; however, Mg and Ca concentrations were slightly elevated relative to the stream sediment (Fig. 3). In addition, sediment samples collected from the non-flowing channel emanating from Goldman Glacier in Taylor Valley have generally similar elemental abundances to Delta Stream sediments, but also exhibit slightly higher concentrations of Mg and Ca compared to sediments collected within Delta Stream (Fig. 3). However, the significant observation of clay minerals in the XRD patterns create difficulties in correlating the observed geochemical signatures in the sediment with the overall mineral abundance trends (Figs. 3 and 4).

In general, the relative abundance of major elements for the mud fraction ($<63 \mu\text{m}$) of sediments is similar for both Wright and Taylor valleys, despite the varied nature of the underlying drift and bedrock for the study sites. Between the Clark Glacier stream and Delta

Stream sample sites, statistically significant differences occur only for elemental concentrations of Ca, Mg, and K ($p < 0.05$), which may be attributed to differences in the percentages of pyroxenes and phyllosilicates (including clay minerals) within each stream (Fig. 4). Overall, sediments collected within Clark Glacier stream contain more pyroxene and a lower percentage of phyllosilicates, whereas Delta Stream sediments contain significantly fewer mafic phases and a high percentage of phyllosilicates (particularly clay minerals) that varies little in abundance along the length of the stream channel.

The variations in sediment chemistry could, therefore, be related to differences in the underlying drift lithologies between Wright and Taylor valleys. Clark Glacier stream traverses a single drift type (Brownworth Drift; Fig. 1), which is underlain by two distinct drift deposits (Loke and Trilogy Drifts) along the course of the stream channel. However, we observed minimal flow and no downcutting in the stream channel during sampling, which implies that substantial contributions from underlying drift deposits are unlikely within the hyporheic zone of Clark Glacier stream and therefore differences in drift lithologies underlying Clark Glacier stream are not a major factor controlling the pronounced downstream increase in pyroxenes and quartz and decrease in phyllosilicates and feldspars. In Taylor Valley, Delta Stream only flows over the Ross Sea drift whereas the Goldman Glacier transect traverses undifferentiated local drift and pre-LGM Ross Sea drift, suggesting that differences in elemental concentrations could be influenced by drift compositions (Fig. 1).

However, the relatively consistent elemental signatures that occur within our Taylor Valley sample sites indicate that eolian contributions likely predominate in redistributing locally

sourced fine-grained material, which concurs with geochemical analyses of eolian material collected within elevated sediment traps throughout Taylor Valley by Deuerling et al. (2014). Variable wind regimes within the hyper-arid climate are known to circulate fine-grained material from the valley drifts onto glacier surfaces and into exposed stream channel beds. This sediment may subsequently become concentrated into meltwater runoff during the limited austral summer, and transported within the weathering environment of the hyporheic zone. In addition, fine-grained material may also be added to the hyporheic zone from eolian deposition within channel snow drifts, as well as from the underlying drift material (Lyons et al., 2003; Bertler et al., 2004; Ayling and McGowan, 2006; Witherow et al., 2006; Williamson et al., 2007; Sabacka et al., 2012; Stumpf et al., 2012; Fortner et al., 2013; Deuerling et al., 2014; Marra et al., 2015). We documented substantial eolian material on top of glaciers in the MDV, particularly on Clark Glacier in Wright Valley, although we were unable to obtain representative samples for comparison (Appendix B).

If eolian processes predominate in the MDV, this may imply that the increase in feldspars and the finest-grained phases (i.e., phyllosilicates) documented within the proximal reaches of Clark Glacier stream transect are related to eolian deposition onto the Clark Glacier surface. At the beginning of stream flow during the melt season, which corresponds to our sampling timeframe in 2010, these sediments would become entrained within the surficial glacier meltwater, and subsequently concentrated within the proximal reaches of the stream transect (Marra et al., 2015). Due to variable flow conditions within MDV streams, the mud (silt and clay) fraction may not have yet been flushed from the proximal region of the stream system due to timing of our sampling. Similarly, in Taylor Valley, the slightly elevated concentrations of Mg

and Ca within samples collected outside the Delta Stream channel suggests that eolian contributions introduced into Delta Stream from the Howard Glacier surface may have lower concentrations of Mg and Ca-bearing minerals relative to the valley-filling drift deposits. Alternatively, elemental loss from weathering or sorting of Mg and Ca-bearing minerals, such as pyroxene, may be occurring within the hyporheic zone associated with Delta Stream, but is not proceeding to a similar extent outside of the hyporheic zone, likely due to reduced contact with moisture.

4.3 Weathering indices of fine-grained sediment

Intensity of chemical weathering in rocks is commonly assessed via the application of weathering indices that evaluate the mobility of major elements (see Price and Velbel, 2003, for a review of these various indices). We utilized four common indices to determine the degree of chemical weathering within and adjacent to the hyporheic zone of the studied Antarctic stream sediments: Chemical Index of Alteration (CIA) (Nesbitt and Young, 1982), Chemical Index of Weathering (CIW) (Harnois, 1988), Plagioclase Index of Alteration (PIA) (Fedo et al., 1995), and Weathering Index of Parker (WIP) (Parker, 1970) (Fig. 5). Values >50 for the CIA, CIW, and PIA typically indicate weathered material, with values increasing with increasing degree of weathering. The WIP differs from the other indices presented here by incorporating aluminum mobility (Parker, 1970; Price and Velbel, 2003) and producing inverse values that decrease as weathering increases, with weathered values typically falling below 100.

Fig. 5. Weathering indices along transect. Drift samples are plotted to the right in each graph for comparison. Samples exhibiting some degree of weathering typically plot above a value of 50 (indicated by the dashed line) for the CIA, CIW, and PIA, whereas “weathered” samples plot below 100 for the WIP. (a) Chemical Index of Alteration ($CIA = 100[Al_2O_3 / (Al_2O_3 + CaO + Na_2O + K_2O)]$). (b) Chemical Index of Weathering ($CIW = 100[Al_2O_3 / (Al_2O_3 + CaO + Na_2O)]$). (c) Plagioclase Index of Alteration ($PIA = 100[(Al_2O_3 - K_2O) / (Al_2O_3 + CaO + Na_2O - K_2O)]$). (d) Weathering Index of Parker ($WIP = 100[(2Na_2O/0.35) + (MgO/0.9) + (2K_2O/0.25) + (CaO/0.7)]$).

As higher surface area may correlate to a higher density of reactive sites on mineral grains for chemical weathering to occur and/or an abundance of fine-grained weathering products such as clay minerals and amorphous and/or nano-sized phases, we also compared the

weathering indices described above to BET surface area and elemental abundances to BET surface area (Figs. 6 and 7; Appendix C) to further investigate the potential role of abundant surface area in chemical weathering in glacial sediments. BET surface area measurements for the fine-grained sediments collected from the stream systems discussed here were previously reported in Marra et al. (2015) and are listed in Appendix C. All weathering indices exhibit a positive correlation with BET surface area, wherein increasingly weathered values are associated with increased surface area for both Wright and Taylor Valley samples. The most pronounced evidence of chemical weathering observed within the mud fraction occurs in Delta Stream sediments collected in 2010, where high surface area values (approximately $>40 \text{ m}^2/\text{g}$) correlate with an increased degree of weathering (Price and Velbel, 2003; Fig. 6). Na and Ca tend to show the most pronounced decrease in abundance within the sediments with the highest measured surface area in Delta Stream, suggesting elemental loss (leaching) is occurring from pyroxenes and feldspars and/or an abundance of fine-grained phyllosilicate phases exist which contain lower concentrations of these two elements (Fig. 7).

Fig. 6. Weathering indices versus BET surface area for each sample. (a) Chemical Index of Alteration. (b) Chemical Index of Weathering. (c) Plagioclase Index of Alteration. (d) Weathering Index of Parker. All plots indicate that samples with higher BET surface area exhibit higher degrees of chemical weathering.

Fig. 7a-g. Whole-rock geochemistry (in weight percent) versus BET surface area for each sample. R^2 values are shown for Clark Glacier stream and Delta Stream samples collected in 2010. Concentrations of Mg and Ca decrease slightly with increasing BET surface area in both Clark and Delta streams (d,e). Concentrations of Ca and Na exhibit the most pronounced loss

with increasing BET surface area, particularly within Delta Stream where BET surface area is $>40 \text{ m}^2/\text{g}$ (e, f).

Chemical weathering indices from sediment samples would ideally be compared to representative “unweathered” parent rock to fully ascertain the extent of weathering. However, the source of the fine-grained material analyzed in this study is from the mixed lithology glacial drift deposits that cover the crystalline basement rock, rather than a single bedrock source. Therefore, we compared the stream mud samples to the mud-size sediment fraction from representative drift samples collected beyond the extent of the hyporheic zone (Fig. 1). Drift samples from both Wright (Brownworth drift) and Taylor (Ross Sea drift) valleys plot within the suggested “fresh” sample range for the CIA, CIW, PIA, and WIP (Fig. 5). However, in Clark Glacier stream, several sediment samples have weathering index values that indicate they are less weathered than the sample of Brownworth drift collected nearby (Fig. 5). In contrast, all of the sediment samples collected from Delta Stream produced weathering index values that exhibit greater degrees of weathering compared to the nearby Ross Sea drift sediment sample.

Whereas CIA, CIW, PIA, and WIP weathering indices were originally designed for application to felsic-intermediate lithologic types and derivative shales, Ohta and Arai (2007) devised a statistical empirical index of chemical weathering that is independent of the composition of the fresh parent rock and thus applicable to felsic, intermediate, and mafic igneous rock types. As the stream sediments collected consist of a range of mixed lithology drift material, we utilized Ohta and Arai’s (2007) method to further assess differences in weathering

within the mud fraction among channel sediments and representative drift samples. In addition, we plotted four samples collected from a stream (Blue Beaver Creek) in the Wichita Mountains of Oklahoma to compare non-glacial weathering in a modern temperate-arid climate to our Antarctic dataset. These sediment samples represent recent Quaternary alluvium and were collected from slackwater fluvial muds in a manner analogous to our Antarctic stream collections. All Wichita samples represent the same size sediment fraction ($<63\ \mu\text{m}$) and were subjected to identical collection and processing methods as utilized in this study (Keiser, 2013; Marra et al., 2014).

The range in mafic to felsic compositions plot along the mafic (M) to felsic (F) poles, and increasingly weathered samples extend toward the weathered (W) pole (Ohta and Arai, 2007; Fig. 8). Antarctic channel sediments plot closer to the mafic apex and are similar in composition to their associated drift samples (Fig. 8). The channel sediments collected from Delta Stream exhibit the highest degree of weathering and a divergence towards the weathered apex compared to the Ross Sea drift sample. The Clark Glacier stream channel sediments exhibit a lesser degree of weathering, but are typically more weathered than the associated Brownworth drift sample. By comparison, sediments from the Wichita Mountains show a higher degree of weathering and the strongest divergence from their associated bedrock sample (Mt. Scott Granite).

Fig. 8. (a) MFW (mafic-felsic-weathered) ternary plot of sediment, drift, and basement rock samples from Antarctica and the Wichita Mountains (Blue Beaver Creek) based on the method of Ohta and Arai (2007). Increasingly weathered samples plot toward the “W” apex. Samples from Delta Stream exhibit a stronger divergence toward the W pole in comparison to Wright Valley samples and their associated drift sample (Ross Sea drift), indicating a greater degree of chemical weathering in this system. Stream samples from Blue Beaver Creek exhibit a higher degree of weathering and the greatest deviation from their associated bedrock sample. (b) Close-up of MFW plot to highlight Antarctic stream and drift samples.

All sediment, drift, and basement rock samples are also plotted on an A-CN-K (Al_2O_3 - $\text{CaO} + \text{Na}_2\text{O}-\text{K}_2\text{O}$) diagram (Nesbitt and Young, 1984) in Fig. 9 for comparison with other studies of chemical weathering in sediments. However, compositional trends in the Antarctic stream sediments are less clear in this plot and tend to remain within a single mixing line, likely

due to the lack of inclusion of Fe and Mg in this plot. On this graph, both the Brownworth and Ross Sea drift samples plot in the same location, and the Delta Stream sediment samples exhibit the widest variation in composition. In contrast, the samples from the Wichita Mountains reveal a clear distinction between bedrock (Mt. Scott Granite) and stream sediments.

Fig. 9. A-CN-K (Al_2O_3 - $CaO + Na_2O$ - K_2O) ternary diagram of sediment, drift, and basement rock samples from Antarctic and the Wichita Mountains (Blue Beaver Creek) in comparison to the Chemical Index of Alteration.

Based on these weathering indices, chemical weathering is occurring in all three streams to variable extents but may be minimally detectable using these geochemical methods in sediments of Antarctic streams and in associated drift samples. In particular, only Delta Stream sediments collected in 2010 show pronounced chemical weathering signatures as measured by weathering indices, and the highest weathering index values correlate to the highest measured BET surface areas (Fig. 6). Within the Clark Glacier stream system, only the sediment sample (CG-2) exhibiting the highest surface area values exhibits some degree of weathering as measured by these indices. In addition, two samples from the Goldman Glacier channel transect (which contained dry sediment and no flowing water during time of sampling) show a small degree of weathering. Associated drift samples from both valleys (Brownworth drift in Wright Valley and Ross Sea drift in Taylor Valley) exhibit relatively “fresh” weathering index values.

A recent study by Bishop et al. (2014) also indicated that surficial sediments collected in and around Lake Brownworth (Wright Valley) and Lake Fryxell (Taylor Valley) exhibit low CIA values for the $<125\ \mu\text{m}$ fraction and plot within the range of relatively “fresh” source rock material. In addition, soil sediment samples collected from the glacial outwash plain of a wet-based glacier (Damma Glacier, Switzerland) also exhibit a limited degree of weathering ($\text{CIA} = 55\text{--}65$), within the range of our high surface area Delta Stream samples (Bernasconi et al., 2011). Surprisingly, CIA values for the $<63\ \mu\text{m}$ fraction of sediments collected from Blue Beaver Creek (Wichita Mountains, OK) range between 59.5–63.9, which is also within the range of our highest surface area samples for Delta Stream where $\text{CIA} = 49.4\text{--}60.2$ (Appendix C). However,

examining the geochemical data in an MFW plot (Fig. 8) reveals clear differences in the extent and nature of chemical weathering in each stream system, wherein all analyzed samples suggest some degree of chemical alteration. In particular, the mud fraction from Delta Stream sediments exhibits the greatest degree of weathering within the analyzed Antarctic stream samples.

Therefore, when examining fluvial sediments, ternary weathering diagrams may be more effective in discerning the degree of chemical weathering rather than using standard weathering index calculations, as even fine-grained sediments contain a mixture of both primary and weathered phases. In addition, plotting in ternary space also enables visualization of the effect of differences in starting compositions.

The positive correlation between BET surface area and weathering index for all analyzed stream mud samples indicates that either the finer-grained material is experiencing more intense and/or faster rates of weathering attributable to higher reactive surface area, and/or that increasingly weathered sediments have higher surface area due to pitting, alteration of grains, and/or production of clay minerals, amorphous, or nanophase weathering products. Gooseff et al. (2002) suggested that amphiboles and plagioclase in the fine fraction of Green Creek (Taylor Valley) stream sediments have a tendency to form etch pits, leading to subsequent disaggregation of particles resulting in higher surface area.

The divergence in weathering signatures between drift and stream sediment samples for both Clark Glacier stream and Delta Stream may suggest that sufficient moisture is not present outside the stream hyporheic zone to promote chemical weathering near the surface at these locations. Alternatively, due to documented eolian distribution of sediments onto glacier

surfaces, chemical alteration and/or dissolution of fine-grained sediment may be occurring within supraglacial meltwater or cryoconite holes on the glacier surface prior to transfer into the stream channel via meltwater flow. Sediment on the glacier surface would likely be subject to longer periods of aqueous alteration compared to sediments in the hyporheic zone as insolation melting occurs before stream flow initiates (Bagshaw et al., 2007; Fountain et al., 2008). However, little fine-grained (clay-sized) sediment occurs in the Clark Glacier stream sediments compared to the nearby glacial drift (Fig. 2). In addition, several of the sediment samples from Clark Glacier stream appear to be less weathered than the Brownworth drift collected outside the stream channel (Fig. 5). Therefore, it is possible that significant quantities of potentially weathered material had not yet been transported from the Clark Glacier surface and into the hyporheic zone due to timing of our sampling (within the first few days of stream flow). However, we did not have a representative sample of surficial sediment from near the terminus of the glacier surface or from cryoconite holes to test this hypothesis. It is also plausible that the observation of weathered material closest to the glacier terminus (Fig. 5) reflects the region of the stream that is most consistently wetted during the austral summer and where discharge is at a maximum (Gooseff et al., 2016), thus promoting enhanced chemical weathering. Alternatively, the apparent lack of weathering observed in the fine-grained fraction of Clark Glacier stream sediments farther down the transect may also suggest that complete dissolution of very fine-grained, weatherable material may be occurring in the dilute meltwaters and therefore leached primary minerals and/or secondary weathering products are not observed within the fine-grained proximal muds.

In addition, it is possible that as surficial glacier melt commences, significant volumes of more felsic-rich sediment are funneled off the glacier surface and concentrated into the proximal reaches of the stream transect. Lower density felsic minerals, such as feldspars and quartz, are more likely to be entrained within the varying wind regimes of the MDV and transported onto glacier surfaces, whereas higher density grains, such as pyroxenes, would remain within the drift sediments and create a residuum of mafic minerals (Speirs et al., 2008). This is similar to processes occur in neighboring Victoria Valley, where preferential entrainment of quartz and feldspars was documented from eolian dune sands, producing a visible lag of mafic minerals (Speirs et al., 2008). Therefore, the pronounced increase in the percentage of feldspars in proximal reaches of Clark Glacier stream may reflect introduction of feldspar-rich fine-grained sediment from the glacier surface during incipient meltwater flow, whereas the increase in pyroxene content down the stream transect may reflect mafic-rich lag which has remained within the drift and stream channel due to its higher density and leading to minimal fluvial and/or eolian transport (Fig. 4).

In Delta Stream, it is likely that incipient production of neoformed mixed layer clays and/or other nanophase weathering products that precipitate from solution, which can be common in glacial regimes (Tranter, 2006), contributed to the high BET surface areas measured in this system. The presence of abundant clays is evident by low-angle broadening of XRD peaks in some Delta Stream sediment samples, indicative of mixed-layer clays (Appendix A). Sediment leaching experiments conducted by Stumpf et al. (2012) also suggest abundant nanophase material is present in the Delta Stream sediments. In this study, Delta Stream sediments released significantly more Si in week-long extraction experiments in both deionized water and HCl

compared to results of leach experiments conducted on Clark Glacier stream sediments. Higher Si release from the Delta Stream samples is likely attributable to more readily soluble Si-bearing phases and/or transport of nanophase colloidal Si phases through the 0.2 μm filters resulting in higher Si concentrations in the extracted solutions (Stumpf et al. 2012). To account for the differences in the two stream systems, it is possible that biological activity in Taylor Valley (Delta Stream) may be facilitating the precipitation of nanoscale clays in localized lower pH environments (i.e., biofilms). We observed significant algal growth in Delta Stream and essentially no biota in Clark Glacier stream (Appendix B). In Clark Glacier stream, most of the silica may stay in solution due to the absence of significant biologic activity. In addition, the silica may not be precipitating in Clark Glacier stream due to a lack of high surface area sediments to serve as heterogeneous nucleation sites (Appendix D).

The higher surface area of Delta Stream sediments collected in 2010 may also reflect accumulation of degraded biotite, chlorite, and/or illite due to low flow conditions during the 2009-2010 austral summer. This is similar to conditions observed by short-term analysis of weathering of muscovite in the hyporheic zone of Green Creek (Maurice et al., 2002). In this study, fresh mica chips buried in the hyporheic zone developed significant etch pits and biofilms over the course of a single melt season (~6 weeks) as a result of chemical weathering and microbial processes. Macht et al. (2011) reported BET surface area values of approximately 41 m^2/g for illite, suggesting progressive weathering (resulting in etch pitting) could enhance the measured surface area of phyllosilicate minerals observed in Delta Stream, in addition to the formation of nanoscale clays. However, the age of the sampled sediments as well as variations in

discharge and wetting of the sediment over the course of multiple melt seasons will impact the extent of weathering, and ultimately changes in surface area, of mineral grains over time.

Fine-grained sediments analyzed from Clark Glacier stream did not exhibit a comparable loss in Na and Ca at high surface area as compared to Delta Stream sediments despite having a similar abundance of feldspars and a higher mafic content (Fig. 7). The differences in elemental abundances between Clark Glacier stream and Delta Stream could be interpreted as reflecting differing weathering processes, where complete dissolution of fine-grained material is occurring in Clark Glacier stream but chemical alteration of the fine-grained fraction is preserved in Delta Stream due to differing flow conditions, where pitting and dissolution of feldspar, pyroxene, and phyllosilicate grains enhance BET surface area. However, the lack of significant accumulation of weathered material in the Clark Glacier stream channel may also reflect the relatively coarser-grained nature of the system (related to the cold-based origin of the Wright Valley drift sediments) or a lack of input of weathered material from the glacier surface into the active hyporheic zone due to timing of sampling. Therefore, in both stream systems, the depositional environment of the drift material (wet and/or cold-based) and hence grain size of the drift sediments, as well as mineral content, eolian dispersal patterns, and stream discharge rates are variable but important factors controlling the distribution of fine-grained, potentially chemically reactive material into the weathering environment of the hyporheic zone.

5. Conclusions

Contrasting weathering indicators observed in the sediment between Wright (Clark Glacier stream) and Taylor (Delta Stream and Goldman Glacier channel transect) Valley streams

indicate that significant differences occur within McMurdo Dry Valley ephemeral streams. In Clark Glacier stream, chemical weathering is minimal in fine-grained ($<63\ \mu\text{m}$) stream sediments despite high solute fluxes in the stream water (Stumpf et al., 2012). These sediments are relatively coarser-grained than Delta Stream sediments, are comprised dominantly of primary minerals, and exhibit a pronounced increase in quartz and pyroxenes and decrease in feldspars along transect. Due to the observed abundance of sediment trapped on the surface of Clark Glacier, we suggest that relatively fresh, felsic-rich sediment is being concentrated into the proximal reaches of the stream transect via transport from surficial glacier melt to explain the increase in feldspars and phyllosilicates near the terminus of the glacier. The relative paucity of clay downstream in this system could reflect: 1) trapping of fine-grained particles on the glacier surface that have not been released into stream channel due to timing of sampling, 2) dissolution of the finest fraction within cryoconite holes atop the glacier, and/or 3) complete dissolution of high surface area material or secondary phases throughout the stream channel such that fine-grained material is not preserved.

Delta Stream sediments contain a much higher percentage of clay, which may be a relict of the former wet-based ice sheets that encroached into Taylor Valley and deposited the underlying Ross Sea drift. These sediments also exhibit the strongest degree of chemical weathering based on various geochemical indices as observed in the samples collected during the 2010 sampling season. The sediments with the highest degree of chemical weathering correlate with higher measured BET surface area ($> 40\ \text{m}^2/\text{g}$). This may reflect accumulation of weathered material in the hyporheic zone due to low-flow conditions during our sampling season, which preserved the fine-grained sediment in the channel and may have enhanced the degradation of

not only primary minerals, but also phyllosilicate phases (i.e., biotite, chlorite, smectite, and illite). In addition, the abundant phyllosilicates in Delta Stream sediments likely contributed to the high BET surface area measurements as well as variations in the observed geochemical trends. However, as in Wright Valley, eolian dispersal patterns, which vary seasonally within and among valleys, and water discharge rates are also critical factors promoting distribution of potentially chemically reactive sediment into the weathering environment of the hyporheic zone, where high discharge rates may flush fine-grained, high surface area material from the stream and promote variable solute loads.

The significant differences in weathering signatures observed between Wright and Taylor Valleys imply that longer-term analysis of chemical weathering in stream sediments of polar climates is warranted to disentangle the links among variable sediment composition, sediment grain sizes, and sediment surface areas in cold-based glacial systems. In particular, further study is warranted to investigate the potential effects of mixed glacial processes (i.e., cold-based glaciation, wet-based glaciation, and grounded ice sheets) on drift sediment processes including grain size, mineralogy, and reactive surface area. Increased understanding of chemical weathering in cold-based glacial systems will provide an important framework for comparison to weathering processes in wet-based glacial systems and to evaluate the potential influence of exposed glacial sediments on the global carbon cycle.

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