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Antarctic streams as a potential source of iron for the Southern Ocean

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ABSTRACT

Due to iron's role in oceanic primary production, there has been great interest in quantifying the importance of Fe in regions where concentrations are very low and macronutrients, nitrate and phosphate, are available. Measurements of filterable (i.e., <0.4 μm) Fe concentrations in streams from Taylor Valley, McMurdo Dry Valleys, Antarctica, suggest that coastal-zone stream Fe input to the Southern Ocean could potentially play an important role in primary production in nearshore regions. Filterable Fe (fFe) data from streams in the McMurdo Dry Valleys were used to represent glacier meltwater that flows through ice-free landscape with the potential of transporting Fe to the Antarctic coastal zone. Estimates of potential fFe flux to the Antarctic Peninsula region using our mean fFe concentration of 10.6 μg L^{-1} combined with an estimate of ice-free area for the Antarctic Peninsula result in an fFe flux of 1.2×10^7 g yr^{-1}. Although small compared to iceberg and aeolian Fe fluxes, future stream input to the Southern Ocean could increase due to glacier retreat and melting, thus increasing the fFe flux from glacier meltwater streams.

INTRODUCTION

Iron often limits oceanic primary production where nutrient (i.e., nitrogen and phosphorus) concentrations are abundant (Moore et al., 2013). Since the seminal work of John H. Martin and coworkers (e.g., Martin et al., 1990), there has been great interest in quantifying the role of Fe in Southern Ocean primary production. Numerous experiments have been conducted that verify the potential importance of Fe in regions where the Fe

concentrations are very low (de Baar et al., 2005; Morris and Charette, 2013). The possibility of CO_2 sequestration from increased Fe addition to the Southern Ocean has also been suggested (Martin et al., 1990; Watson et al., 2000).

Considering that the atmospheric flux of Fe to the Antarctic circumpolar region is the lowest globally (Jickells et al., 2005), it had been thought prior to the mid-2000s that the majority of Fe was supplied by the up- welling of deeper waters (Watson et al., 2000). Later work has indicated that glacier runoff and glacially derived sediment also contribute substantial amounts of Fe to the polar oceans and provide sufficient sources to fertilize increased primary production in the Southern Ocean (Statham et al., 2008; Raiswell, 2011). A comprehensive review of Fe input into the Southern Ocean is found in Raiswell and Canfield (2012). They have demonstrated that between 770×10^9 g yr^{-1} and 1300×10^9 g yr^{-1} of filter- able Fe (henceforth fFe, i.e., Fe in solution that passes through a 0.4 μm filter) enters the Southern Ocean, the large majority coming from icebergs. Meltwater inputs for fFe into the Southern Ocean were determined to be only a small percentage of the total at $0.030–3.0 \times 10^9$ g yr^{-1} (Wadham et al., 2013). Yet even more recent estimates suggest that glacial runoff of potentially bioavailable nanoparticle Fe within the suspended sediment fraction is only an order of magnitude lower than the iceberg flux (Hawkings et al., 2014). It has also been recognized that the bioavailable particulate Fe from glacier runoff may vary greatly and thus complicate the quantification of bioreactive Fe into the polar oceans (Hopwood et al., 2014). The Fe concentration of groundwater input derived from acid rock drainage from King George Island, South Shetland Islands, into the ocean extrapolated onto the entire ice-free coastline of Antarctica is the same order of magnitude of input to the Southern Ocean as glacier or aeolian sources (Dold et al., 2013). Nonetheless, relatively little information exists on the concentrations of fFe in streams in the ice-free regions of Antarctica and how this stream source would compare to the other potential sources. In this paper, we present the first estimates of fFe concentrations derived from a solely ice-free, terrestrial water source from the Antarctic with data from the McMurdo Dry Valleys (~78°S).

STUDY AREA

The McMurdo Dry Valleys (MDV) are the largest ice-free region in Antarctica. The

landscape consists of glaciers, perennial streams that flow 4–10 weeks per year, ice-covered lakes, and soil. The soils are derived from tills of various ages deposited by both the West and East Antarctic Ice Sheets and consist of relatively unweathered components of the various local rock types, including the Precambrian and Cambrian crystalline basement rocks, the Jurassic Ferrar dolerite, the Permian Beacon sandstone and mudstone, and the recent McMurdo volcanic series (Hall and Denton, 2000). There is essentially no groundwater and no overland flow, as the primary source of water is glacier melt that moves through permanent stream channels (McKnight et al., 1999). The ecosystem is dominated by microorganisms, and there are no vascular plants. The MDV are considered to be a polar desert with a mean annual temperature near –20°C, a mean austral summer (December, January, February) temperature near –4 °C, and a mean annual precipitation of 3 cm yr^{-1} water equivalent (MCM-LTER, 2013; Doran et al., 2002; Fountain et al., 2010). Since 1993, Taylor Valley has been the primary focus area of the McMurdo Dry Valleys Long-Term Ecological Research (MCM-LTER) program. The geochemistry, hydrology, and biology of the streams of Taylor Valley have been described in detail (Welch et al., 2010; McKnight et al., 1999). Additionally, Blood Falls is a hypersaline, very Fe-rich discharge in contact with the Taylor Glacier in Taylor Valley (Mikucki et al., 2009). Samples from streams that are associated with Blood Falls with extremely high fFe concentrations were excluded from all calculations and subsequent discussions because they are probably not representative of glacier meltwater streams in the MDV and other ice-free regions on the continent.

SAMPLING AND ANALYSIS

Stream water samples from Taylor Valley were collected as part of the MCM-LTER program during the flow season from the end of November 2012 to the end of January 2013. Most streams were sampled on a weekly basis, while ungauged streams were sampled less frequently. Samples were collected upstream of the stream gauge or near the mouth of the stream if not gauged. Samples were filtered within hours of collection, using 0.4 µm Nuclepore polycarbonate membrane filters, into polyethylene bottles that were rinsed with 1% HCl solution and then rinsed five times with ultra-pure water. The samples were acidified to 0.1% with Ultrex nitric acid, placed in clean polyethylene

bags, and returned to The Ohio State University (USA) where they were analyzed for fFe. It has now been clearly recognized that the fraction of Fe that passes through a 0.4/0.45 □m filter contains both nanoparticles and colloids, and only a small percent- age of it is truly “dissolved” (Statham et al., 2008; Raiswell and Canfield, 2012). Therefore, we only compare our data to other information where 0.4/0.45 µm filtration has been used. The acidification of samples after filtration ensured that colloids and nanoparticles were in suspension and thus analyzed alongside aqueous Fe species by our analytical technique.

A modified version of the FerroZine method was used to determine the fFe concentration of all samples (Stookey, 1970; see the GSA Data Repository[1]). Reagent blanks were analyzed to determine background absorbance values. The mean absorbance value of the reagent blanks was subtracted from measured absorbance values of the standards and samples to account for the blank signal, and the calibration curve was forced through zero. Precision of the measurements was <5% based on the average relative percent difference between duplicates. A low detection limit was attained by using a cylindrical spectrophotometric cell with a 10 cm path length for all analyses in order to maximize the signal response at low concentrations. The detection limit was calculated as the concentration of 3× the standard deviation of five reagent blanks plus the difference between the highest observed blank and the mean blank, and is ~2 µg L^{-1}. Filtration blanks from previous sampling years were analyzed, and all six measurements fell below the limit of detection.

RESULTS AND DISCUSSION

Results

Filterable Fe data are provided in the Data Repository. All of the fFe data from Taylor Valley are presented in Figure 1. The mean fFe con- centration of all samples from Taylor Valley was 10.6 µg L^{-1} (n = 143). Samples measured at or below the detection limit but above the mean blank were included in calculating the mean fFe concentration to represent the low concentrations present in these systems. The values presented here are similar to those reported by Green et al. (2005) for the Onyx River in Wright Valley, north of Taylor Valley in MDV, at a mean of 13 µg L^{-1} (n = 12), and by

Webster-Brown and Webster (2007) at 3 μg L^{-1} and 13 μg L^{-1}, as well as values for waters in northern Victoria Land at 6.7 μg L^{-1} (Bargagli, 2000).

Source of the Iron

The fFe in the streams of MDV comes from chemical weathering of either the stream channel sediments or the aeolian materials on glacier surfaces, as subglacial flow is negligible. Extensive chemical weathering in the hyporheic zones of the stream channels in MDV has been thoroughly documented (Gooseff et al., 2002). The accumulation of aeolian material on glacier surfaces changes the albedo in depressions and, with substantial melting, can form cryoconites (Tranter et al., 2004). Within these cryoconites and the drainage systems that they form, salt dissolution and chemical weathering can occur (Bagshaw et al., 2007). Recent work has determined the presence of Fe in this aeolian material, but only a very small fraction of the total Fe is water soluble at 20–220 ng g^{-1} (Deuerling, 2010).

Total Fe concentrations from the Onyx River bulk sediments ranged from 5.8 mg g^{-1} to 12 mg g^{-1} (Webster-Brown and Webster, 2007). In MDV, we believe the majority of Fe observed in streams comes from chemical weathering in the hyporheic zones. This notion is supported by previous work that indicated streams with larger hyporheic zones in Taylor Valley have increasing fFe concentrations during the falling limb of the hydrograph, suggesting hyporheic zone draining (Fortner et al., 2013). In addition, biological processes can affect nutrient dynamics and redox conditions in the hyporheic zones (McKnight et al., 2004) and may aid in solubilizing Fe through Fe^{3+} reduction.

Suspended sediment data for the Taylor Valley streams are very limited. However, values ranging from 0.7 to 362 mg L^{-1} of suspended sediment have been previously observed (Table DR2 in the Data Repository). Assuming that the suspended sediment in streams is chemically similar to sediment from aeolian sources, these values and the water-soluble Fe values from Deuerling (2010), mentioned above, indicate that the contribution of fFe from aeolian sources would be ≤0.08 μg L^{-1}. Yet streams that have flowed over recently deposited aeolian material can have much higher

fFe concentrations (Fortner et al., 2013). Thus high rock-water ratios and increased rock-water interactions lead to measurable fFe in these waters. There is little information on the concentration of Fe in Antarctic continental streams other than that in the MDV, in part due to their difficulty of access. The other data from the northern Antarctic Peninsula region include data from Signy Island, where fFe averaged 17 μg L^{-1} (Hodson et al., 2010), and King George Island, where dissolvable and fFe in streams averaged 67 and 17 μg L^{-1}, respectively (Nedzarek et al., 2014). These fFe concentrations are ~60% higher than what we observed in the MDV. Unlike in the MDV, there has been very little work to assess the hydrologic nature of these streams and the source of fFe to them. Because of the warmer mean annual temperatures, differing permafrost dynamics, and potential for overland flow, chemical weathering can occur throughout the watershed and not just in the hyporheic zones of the streams (Lyons et al., 2013). Therefore, we conclude that the fFe in MDV streams is primarily from stream channel, and likely hyporheic zone, weathering, but there may be a contribution from the solubilization of fFe from aeolian materials where they are freshly deposited.

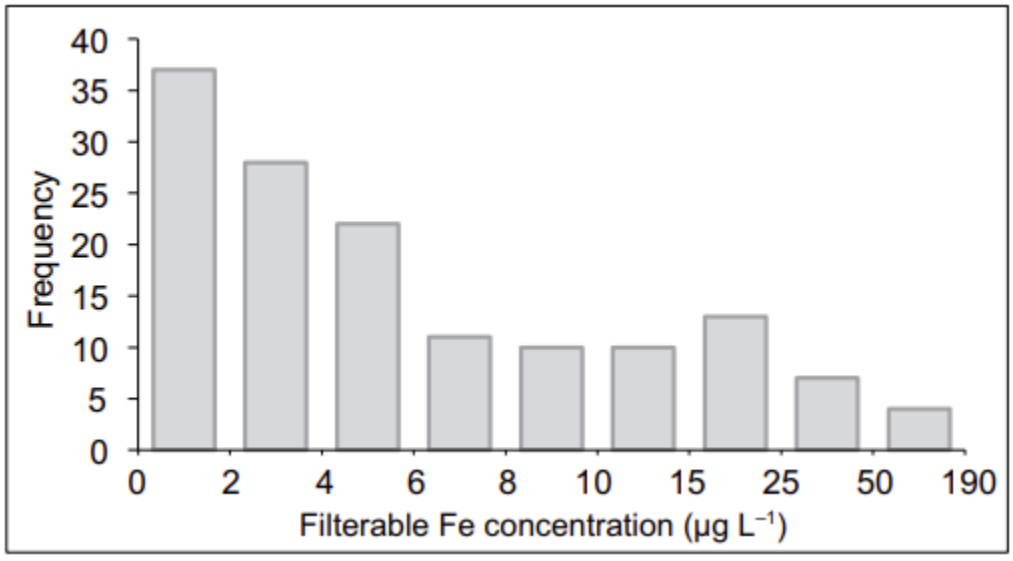

Figure 1. Distribution of filterable Fe concentrations of individual samples from Taylor Valley, McMurdo Dry Valleys, Antarctica. Note changes in *x*-axis scale at 10, 25, and 50 μg L^{-1}.

Potential Source of Stream Fe to the Southern Ocean

As noted above, Fe is a potential limitation to primary production. In many cases, fFe concentrations in Southern Ocean waters are much be- low the detection limit used

in our study, ~2 μg L^{-1}. However, in both the Ross Sea sector and near the Antarctic Peninsula, the fFe concentrations increase approaching the Antarctic continent (Coale et al., 2005; Sañudo-Wilhelmy et al., 2002). These observations clearly suggest a substantial input of fFe from the continent even though a significant fraction of continentally derived Fe can be removed close to shore (Schroth et al., 2014; Alderkamp et al., 2015). Although this increase close to shore could be sustained by input from continental shelf sediments (Dulaiova et al., 2009), meltwater runoff likely also contributes Fe to these waters. Previous work has suggested that iceberg and glacier runoff sources are quantitatively important (Raiswell et al., 2008; Statham et al., 2008; Death et al., 2013). Furthermore, glacier meltwater plumes have been previously detected in coastal Antarctica (Dierssen et al., 2002). Both of these potential sources are difficult to quantify. Recent work may also indicate that input from glacier runoff could originate from subglacial flow related to ice-shelf melting, thus adding an important third source (Wadham et al., 2013). Each of these three ice melt sources may have very different Fe concentrations. For example, subglacial flow could potentially contain high fFe concentrations due to enhanced rock-water interactions, increasing the chemical weathering flux with reducing conditions (Wadham et al., 2010).

Clearly there is great difficulty in assessing the amount of meltwater actually entering the ocean. From estimates of ice mass loss from Antarctica to the Southern Ocean, we are unable to determine how much of the loss was due to calving and how much was from melt. In addition, the majority of the meltwater loss was not from water that had passed through proglacial landscape, while some melt percolated into the subsurface and refroze. Jacobs et al. (2002) estimated from oceanographic measurements a meltwater input of ~0.4– 50 × 10^{12} L yr^{-1}, while Pattyn (2010) put the figure at 32.5–97.5 × 10^{12} L yr^{-1}. Quantification of actual meltwater from non–ice shelf sources has been estimated recently as 32 × 10^{12} L yr^{-1}, with the majority originating from the Peninsula region (Kuipers Munneke et al., 2012). Earlier estimates from the Peninsula region were higher (Vaughan, 2006). Values of 11 × 10^{12} L yr^{-1} have been estimated for the Ross Sea region (Kuipers Munneke et al., 2012). Additionally, there are large variations in values from year to year.

The current estimated subsurface flux of dissolved (filterable through 0.2 μm) Fe is 0.45×10^9 g yr^{-1} for the coast of Antarctica (Dold et al., 2013). The nearshore aeolian flux of total dissolvable Fe determined on unfiltered samples of Antarctic seasonal sea ice is 0.3×10^9 g yr^{-1} (Ed- wards and Sedwick, 2001). Inputs of Fe from melting at the surface and base of marine terminal glaciers also contribute biologically significant amounts (Gerringa et al., 2012). Although this flux is small compared to the iceberg and aeolian fluxes for the entire Southern Ocean (Raiswell and Canfield, 2012), it is undoubtedly important in the nearshore regions of the continent. Work in the Antarctic Peninsula region suggests that glacier meltwater can be observed at times ~100 km offshore (Dierssen et al., 2002), suggesting that this source of Fe may be important even beyond the coastal zone (Gerringa et al., 2012).

The majority of the streams in the MDV currently flow into closed-basin lakes. Using stream-gauging records and the measurement of lake level changes, the warmest summer between 1993 and 2014 (i.e., 2001–2002) produced ~3.2×10^{10} L of measured glacier melt in Taylor and Wright Valleys. This volume of melt and our mean fFe value (10.6 μg L^{-1}) along with the ice-free area of the central MDV (3000 km^2) from Levy (2013) produced a stream fFe yield of ~1.1×10^2 g km^{-2} yr^{-1}. We can apply our calculated fFe yield from the MDV to other ice-free regions in Antarctica. However, there is a range of values for the area of ice-free domains, making it difficult to quantify the potential fFe flux to the ocean. For example, using the ice-free area for the Antarctic continent from Cary et al. (2010), the potential fFe flux is only 6.2×10^6 g yr^{-1}. However, using the ice-free area of the Antarctic Peninsula from Bindschadler (2006), we calculate a flux in this region alone of 1.2×10^7 g yr^{-1}. If the total ice-free area of East Antarctica from Bindschadler (2006) is utilized, we obtain a potential fFe flux of 2.3×10^8 g yr^{-1}. Therefore, we are unable to compare the present- day subaerial flux from the continent. However, in some areas such as the Antarctic Peninsula where glaciers are retreating rapidly, fFe from stream water could be important locally or even regionally.

Recent work has projected that in the MDV region, glacier melting will increase and subsurface ice and permafrost that underlie a large portion of the lower elevation regions of MDV will be at “risk” as the climate warms (Fountain et al., 2014). In the Arctic, the

deepening of the thawed active layer leads to increases in stream fFe fluxes at the end of the melt season (Barker et al., 2014). So as the climate warms around the edges of the Ant- arctic continent, ice-free areas increase in size, and active layers deepen, the Fe flux from subaerial streams will also increase. This Fe will serve as an important source of Fe to the coastal Southern Ocean.

Notes

[1]GSA Data Repository item 2015336, FerroZine method modifications, filterable Fe data and analysis, and suspended sediment data, is available online at www.geosociety.org/pubs/ft2015.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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REFERENCES CITED

Alderkamp, A., et al., 2015, Fe availability drives phytoplankton photosynthesis rates during spring bloom in the Amundsen Sea Polynya, Antarctica: Elementa: Science of the Anthropocene. v. 3, 000043, doi:10.12952/journal.elementa.000043.

Bagshaw, E.A., Tranter, M., Fountain, A.G., Welch, K.A., Basagic, H., and Lyons, W.B., 2007, Biogeochemical evolution of cryoconite holes on Canada Glacier, Taylor Valley, Antarctica: Journal of Geophysical Research, v. 112, G04S35, doi:10.1029/2007JG000442.

Bargagli, R., 2000, Trace metals in Antarctica related to climate change and in- creasing human impact: Reviews of Environmental Contamination and Toxi- cology, v.

166, p. 129–173.

Barker, A.J., Douglas, T.A., Jacobson, A.D., McClelland, J.W., Ilgen, A.G., Khosh, M.S., Lehn, G.O., and Trainor, T.P., 2014, Late season mobilization of trace metals in two small Alaskan arctic watersheds as a proxy for landscape scale permafrost active layer dynamics: Chemical Geology, v. 381, p. 180–193, doi:10.1016/j.chemgeo.2014.05.012.

Bindschadler, R., 2006, The environment and evolution of the West Antarctic ice sheet: Setting the stage: Philosophical Transactions of the Royal Society of London, ser. A, v. 364, p. 1583–1605, doi:10.1098/rsta.2006.1790.

Cary, S.C., McDonald, I.R., Barrett, J.E., and Cowan, D.A., 2010, On the rocks: The microbiology of Antarctic Dry Valley soils: Nature Reviews: Microbiology, v. 8, p. 129–138, doi:10.1038/nrmicro2281.

Coale, K.H., Gordon, R.M., and Wang, X., 2005, The distribution and behavior of dissolved and particulate iron and zinc in the Ross Sea and Antarctic circumpolar current along 170°W: Deep-Sea Research: Part I, Oceanographic Research Papers, v. 52, p. 295–318, doi:10.1016/j.dsr.2004.09.008.

Death, R., Wadham, J.L., Monteiro, F., Le Brocq, A.M., Tranter, M., Ridgwell, A., Dutkiewicz, S., and Raiswell, R., 2013, Antarctic Ice Sheet fertilises the Southern Ocean: Biogeosciences Discussions, v. 10, p. 12,551–12,570, doi: 10.5194/bgd-10-12551-2013.

de Baar, H.J.W., et al., 2005, Synthesis of iron fertilization experiments: From the Iron Age in the Age of Enlightenment: Journal of Geophysical Research, v. 110, C09S16, doi:10.1029/2004JC002601.

Deuerling, K.M., 2010, Aeolian sediments of the McMurdo Dry Valleys, Antarctica [M.S. thesis]: Columbus, The Ohio State University, 178 p.

Dierssen, H.M., Smith, R.C., and Vernet, M., 2002, Glacial meltwater dynamics in coastal waters west of the Antarctic peninsula: Proceedings of the National Academy of Sciences of the United States of America, v. 99, p. 1790–1795, doi:10.1073/pnas.032206999.

Dold, B., Gonzalez-Toril, E., Aguilera, A., Lopez-Pamo, E., Cisternas, M.E., Bucchi, F., and Amils, R., 2013, Acid rock drainage and rock weathering in Antarctica:

Important sources for iron cycling in the Southern Ocean: Environ- mental Science & Technology, v. 47, p. 6129–6136, doi:10.1021/es305141b.

Doran, P.T., McKay, C.P., Clow, G.D., Dana, G.L., Fountain, A.G., Nylen, T., and Lyons, W.B., 2002, Valley floor climate observations from the McMurdo dry valleys, Antarctica, 1986–2000: Journal of Geophysical Research, v. 107, 4772, doi:10.1029/2001JD002045.

Dulaiova, H., Ardelan, M.V., Henderson, P.B., and Charette, M.A., 2009, Shelf-derived iron inputs drive biological productivity in the southern Drake Passage: Global Biogeochemical Cycles, v. 23, GB4014, doi:10.1029/2008GB003406.

Edwards, R., and Sedwick, P., 2001, Iron in East Antarctic snow: Implications for atmospheric iron deposition and algal production in Antarctic waters: Geo- physical Research Letters, v. 28, p. 3907–3910, doi:10.1029/2001GL012867.

Fortner, S.K., Lyons, W.B., and Munk, L., 2013, Diel stream geochemistry, Taylor Valley, Antarctica: Hydrological Processes, v. 27, p. 394–404, doi:10.1002/hyp.9255.

Fountain, A.G., Nylen, T.H., Monaghan, A., Basagic, H.J., and Bromwich, D., 2010, Snow in the McMurdo Dry Valleys, Antarctica: International Journal of Climatology, v. 30, p. 633–642.

Fountain, A.G., Levy, J.S., Gooseff, M.N., and Van Horn, D., 2014, The McMurdo Dry Valleys: A landscape on the threshold of change: Geomorphology, v. 225, p. 25–35, doi:10.1016/j.geomorph.2014.03.044.

Gerringa, L.J.A., Alderkamp, A., Laan, P., Thuroczy, C., De Baar, H.J.W., Mills, M.M., van Dijken, G.L., van Haren, H., and Arrigo, K.R., 2012, Iron from melting glaciers fuels the phytoplankton blooms in Amundsen Sea (Southern Ocean): Iron biogeochemistry: Deep-Sea Research: Part II, Topical Studies in Oceanography, v. 71–76, p. 16–31, doi:10.1016/j.dsr2.2012.03.007.

Gooseff, M.N., McKnight, D.M., Lyons, W.B., and Blum, A.E., 2002, Weathering reactions and hyporheic exchange controls on stream water chemistry in a glacial meltwater stream in the McMurdo Dry Valleys: Water Resources Research, v. 38, p. 15-1–15-17.

Green, W.J., Stage, B.R., Preston, A., Wagers, S., Shacat, J., and Newell, S., 2005, Geochemical processes in the Onyx River, Wright Valley, Antarctica: Major ions,

nutrients, trace metals: Geochimica et Cosmochimica Acta, v. 69, p. 839–850, doi:10.1016/j.gca.2004.08.001.

Hall, B.L., and Denton, G.H., 2000, Radiocarbon chronology of Ross Sea drift, eastern Taylor Valley, Antarctica: Evidence for a grounded ice sheet in the Ross Sea at the last glacial maximum: Geografiska Annaler: Series A, Physical Geography, v. 82, p. 305–336, doi:10.1111/j.0435-3676.2000.00127.x.

Hawkings, J.R., Wadham, J.L., Tranter, M., Raiswell, R., Benning, L.G., Statham, P.J., Tedstone, A., Nienow, P., Lee, K., and Telling, J., 2014, Ice sheets as a significant source of highly reactive nanoparticulate iron to the oceans: Nature Communications, v. 5, 3929, doi:10.1038/ncomms4929.

Hodson, A., Heaton, T., Langford, H., and Newsham, K., 2010, Chemical weathering and solute export by meltwater in a maritime Antarctic glacier basin: Biogeochemistry, v. 98, p. 9–27, doi:10.1007/s10533-009-9372-2.

Hopwood, M.J., Statham, P.J., Tranter, M., and Wadham, J.L., 2014, Glacial flours as a potential source of Fe(II) and Fe(III) to polar waters: Biogeochemistry, v. 118, p. 443–452, doi:10.1007/s10533-013-9945-y.

Jacobs, S.S., Giulivi, C.F., and Mele, P.A., 2002, Freshening of the Ross Sea during the late 20th century: Science, v. 297, p. 386–389, doi:10.1126/science.1069574.

Jickells, T.D., et al., 2005, Global iron connections between desert dust, ocean biogeochemistry, and climate: Science, v. 308, p. 67–71, doi:10.1126/science.1105959.

Kuipers Munneke, P., Picard, G., van den Broeke, M.R., Lenaerts, J.T.M., and van Meijgaard, E., 2012, Insignificant change in Antarctic snowmelt volume since 1979: Geophysical Research Letters, v. 39, L01501, doi:10.1029/2011GL050207.

Levy, J., 2013, How big are the McMurdo Dry Valleys?: Estimating ice-free area using Landsat image data: Antarctic Science, v. 25, p. 119–120, doi:10.1017/S0954102012000727.

Lyons, W.B., Welch, K.A., Welch, S.A., Camacho, A., Rochera, C., Michaud, L., deWit, R., and Carey, A.E., 2013, Geochemistry of streams from Byers Pen- insula, Livingston Island: Antarctic Science, v. 25, p. 181–190, doi:10.1017/S0954102012000776.

Martin, J.H., Gordon, R.M., and Fitzwater, S.E., 1990, Iron in Antarctic waters:

Nature, v. 345, p. 156–158, doi:10.1038/345156a0.

McKnight, D.M., Niyogi, D.K., Alger, A.S., Bomblies, A., Conovitz, P.A., and Tate, C.M., 1999, Dry valley streams in Antarctica: Ecosystems waiting for water: BioScience, v. 49, p. 985–995, doi:10.2307/1313732.

McKnight, D.M., Runkel, R.L., Tate, C.M., Duff, J.H., and Moorhead, D.L., 2004, Inorganic N and P dynamics of Antarctic glacial meltwater streams as controlled by hyporheic exchange and benthic autotrophic communities: Journal of the North American Benthological Society, v. 23, p. 171–188, doi:10.1899/0887593(2004)023<0171:INAPDO>2.0.CO;2.

MCM-LTER (McMurdo Dry Valleys Long-Term Ecological Research Program), 2013, MCM meteorology data: http://www.mcmlter.org/queries/met/met_home.jsp (accessed October 2013).

Mikucki, J.A., Pearson, A., Johnston, D.T., Turchyn, A.V., Farquhar, J., Schrag, D.P., Anbar, A.D., Priscu, J.C., and Lee, P.A., 2009, A contemporary microbially maintained subglacial ferrous “ocean”: Science, v. 324, p. 397–400, doi:10.1126/science.1167350.

Moore, C.M., et al., 2013, Processes and patterns of oceanic nutrient limitation: Nature Geoscience, v. 6, p. 701–710, doi:10.1038/ngeo1765.

Morris, P.J., and Charette, M.A., 2013, A synthesis of upper ocean carbon and dissolved iron budgets for Southern Ocean natural iron fertilisation studies: Deep-Sea Research: Part II, Topical Studies in Oceanography, v. 90, p. 147– 157, doi:10.1016/j.dsr2.2013.02.001.

Nedzarek, A., Torz, A., and Drost, A., 2014, Selected elements in surface waters of Antarctica and their relations with the natural environment: Polar Re- search, v. 33, 21417, doi:10.3402/polar.v33.21417.

Pattyn, F., 2010, Antarctic subglacial conditions inferred from a hybrid ice sheet/ ice stream model: Earth and Planetary Science Letters, v. 295, p. 451–461, doi:10.1016/j.epsl.2010.04.025.

Raiswell, R., 2011, Iceberg-hosted nanoparticulate Fe in the Southern Ocean: Mineralogy, origin, dissolution kinetics and source of bioavailable Fe: Deep- Sea Research: Part II, Topical Studies in Oceanography, v. 58, p. 1364–1375,

doi:10.1016/j.dsr2.2010.11.011.

Raiswell, R., and Canfield, D.E., 2012, The iron biogeochemical cycle past and present: Geochemical Perspectives, v. 1, p. 1–220, doi:10.7185/geochempersp.1.1.

Raiswell, R., Benning, L.G., Tranter, M., and Tulaczyk, S., 2008, Bioavailable iron in the Southern Ocean: The significance of the iceberg conveyor belt: Geochemical Transactions, v. 9, doi:10.1186/1467-4866-9-7.

Sañudo-Wilhelmy, S.A., Olsen, K.A., Scelfo, J.M., Foster, T.D., and Flegal, A.R., 2002, Trace metal distributions off the Antarctic Peninsula in the Weddell Sea: Marine Chemistry, v. 77, p. 157–170, doi:10.1016/S0304-4203(01) 00084-6.

Schroth, A.W., Crusius, J., Hoyer, I., and Campbell, R., 2014, Estuarine removal of glacial iron and implications for iron fluxes to the ocean: Geophysical Research Letters, v. 41, p. 3951–3958, doi:10.1002/2014GL060199.

Statham, P.J., Skidmore, M., and Tranter, M., 2008, Inputs of glacially derived dissolved and colloidal iron to the coastal ocean and implications for primary productivity: Global Biogeochemical Cycles, v. 22, GB3013, doi:10.1029/2007GB003106.

Stookey, L.L., 1970, Ferrozine: A new spectrophotometric reagent for iron: Analytical Chemistry, v. 42, p. 779–781, doi:10.1021/ac60289a016.

Tranter, M., Fountain, A.G., Fritsen, C.H., Lyons, W.B., Priscu, J.C., Statham, P.J., and Welch, K.A., 2004, Extreme hydrochemical conditions in natural microcosms entombed within Antarctic ice: Hydrological Processes, v. 18, p. 379–387, doi:10.1002/hyp.5217.

Vaughan, D.G., 2006, Recent trends in melting conditions on the Antarctic Peninsula and their implications for ice-sheet mass balance and sea level: Arctic, Antarctic, and Alpine Research, v. 38, p. 147–152, doi:10.1657/1523-0430 (2006)038[0147:RTIMCO]2.0.CO;2.

Wadham, J.L., Tranter, M., Skidmore, M., Hodson, A.J., Priscu, J., Lyons, W.B., Sharp, M., Wynn, P., and Jackson, M., 2010, Biogeochemical weathering under ice: Size matters: Global Biogeochemical Cycles, v. 24, GB3025, doi:10.1029/2009GB003688.

Wadham, J.L., Death, R., Monteiro, F.M., Tranter, M., Ridgwell, A., Raiswell, R.,

and Tulaczyk, S., 2013, The potential role of the Antarctic Ice Sheet in global biogeochemical cycles: Earth and Environmental Science Trans- actions of the Royal Society of Edinburgh, v. 104, p. 55–67, doi:10.1017/S1755691013000108.

Watson, A.J., Bakker, D.C.E., Ridgwell, A.J., Boyd, P.W., and Law, C.S., 2000, Effect of iron supply on Southern Ocean CO_2 uptake and implications for glacial atmospheric CO_2: Nature, v. 407, p. 730–733, doi:10.1038/35037561.

Webster-Brown, J.G., and Webster, K.S., 2007, 2007, Trace metals in cyanobacterial mats, phytoplankton and sediments of the Lake Vanda region, Antarctica: Antarctic Science, v. 19, p. 311–319, doi:10.1017/S0954102007000417.

Welch, K.A., Lyons, W.B., Whisner, C., Gardner, C.B., Gooseff, M.N., McK- night, D.M., and Priscu, J.C., 2010, Spatial variations in the geochemistry of glacial meltwater streams in the Taylor Valley, Antarctica: Antarctic Science, v. 22, p. 662–672, doi:10.1017/S0954102010000702.