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Geochemistry of aeolian material from the McMurdo Dry Valleys, Antarctica: Insights into Southern Hemisphere dust sources

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A B S T R A C T

In the Southern Hemisphere, the major sources of dust and other aeolian materials are from Patagonia, South Africa, Australia, and New Zealand. Dust from Patagonia and New Zealand has been identified in ice cores throughout Antarctica, suggesting that during arid and windy periods, such as glacial periods, dust can be entrained and transported onto the continent. However, little information exists on modern Antarctic dust sources, transport, and its role in the Southern Hemisphere dust cycle. We present the first geochemical characterization of aeolian materials collected at five heights (between 5 cm and 100 cm) above the surface in four valleys within the McMurdo Dry Valleys, the largest ice-free area in Antarctica. Our mineralogy data indicate that these materials are primarily derived from local rocks of the McMurdo Volcanics, Ferrar Dolerite, Beacon Sandstone and Granite Harbor Intrusives, with varying contributions of each rock type dependent on the valley location. While major oxide, trace element and rare earth element data show that low elevation and coastal locations (with respect to the Ross Sea) are dominated by local sources, high elevation and inland locations have accumulated both local materials and dust from other distant Southern Hemisphere sources. This far-traveled material may not be accumulating today, but represents a paleo source that is resuspended from the soils. By geochemically "fingerprinting" aeolian materials from the MDV, we can better inform future studies on the transport of materials within Antarctica and between Southern Hemisphere land masses.

1. Introduction

The Transantarctic Mountains (TAM) traverse the Antarctic continent and separate the East Antarctic Ice Sheet (EAIS) from the West Antarctic Ice Sheet (WAIS). The TAM act as an elevational boundary for the EAIS and impede ice flow towards the Ross Sea (Fig. 1). This physical barrier creates ice free areas, which may contribute dust to remote inland Antarctic locations. The McMurdo Dry Valleys (MDV), located in Southern Victoria Land, East Antarctica (Fig. 1), constitute the largest contiguous ice-free area on the Antarctic continent. In these cold desert environments, dust is generated, and its mass transport rate can be significantly higher than in regions with more temperate climates (McKenna Neuman, 2004). This dust is not only deposited in areas around the MDV (Delmonte et al., 2010a, 2010b; Witherow et al., 2006), but can potentially be transported to other Southern Hemisphere regions, though little work exists on quantifying the influence of modern Antarctic aeolian material on other continents (see Bullard, 2017).

Evidence from ice cores throughout Antarctica shows that Patagonia and Australia were dominant sources of particulate material at Talos Dome (72°48′S, 159°06′E) (Albani et al., 2012; Baccolo et al., 2018; Delmonte et al., 2017, 2008) and Dome C (Basile et al., 1997; De Deckker et al., 2010; Delmonte et al., 2007; Gabrielli et al., 2010) during the Last Glacial Maximum (LGM). During interglacial periods, less dust from other continents is transported to Antarctica (Albani et al., 2012). Local dust de-

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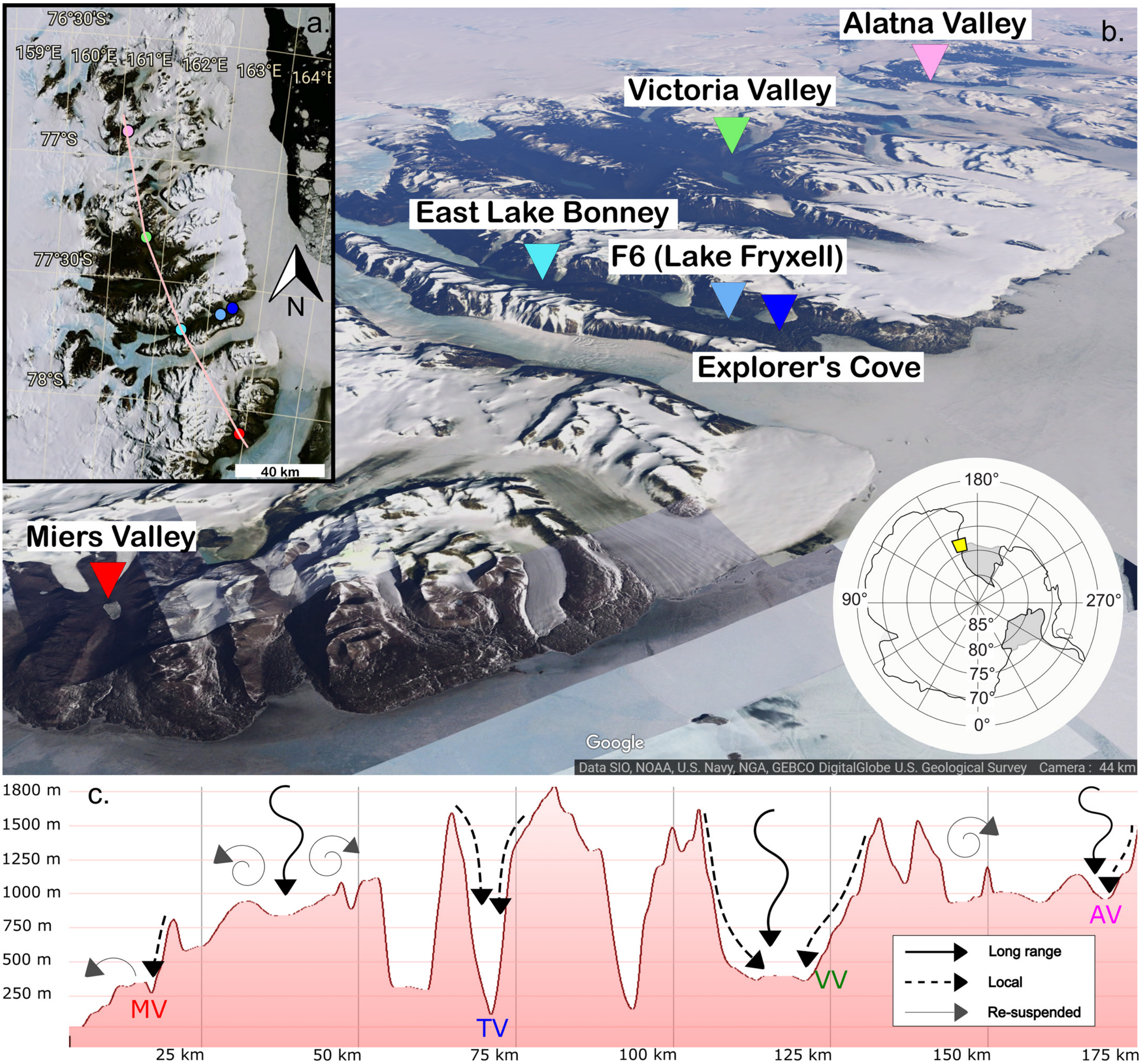

Fig. 1. Satellite images and map of study areas within the McMurdo Dry Valleys, East Antarctica (a). A 3-dimensional map shows the various surface features of the Dry Valleys, including several peaks, glacial tongues, lakes with ephemeral streams, and exposed soils (b). An elevational transect from Miers Valley (MV) through Taylor and Victoria Valleys (TV and VV respectively) up until Alatna Valley (AV) shows the relative elevations of MDV valleys and landscape features (c). Arrows represent different mechanisms of aeolian material transport following conventions of Marx et al. (2018).

position could be of greater importance, especially for periphery regions and during interglacial periods (Delmonte et al., 2013).

In order to better understand the influence of dust on the global climate, sources of aeolian material need to be identified and characterized. Dust in Antarctic ice cores has been analyzed for many constituents, including both isotopic ($^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$) (e.g. Blakowski et al., 2016; Delmonte et al., 2010a) and rare earth element (REE) (e.g. Gabrielli et al., 2010; Wegner et al., 2012) signatures which have been utilized to discern dust provenance. These previous studies suggested that, based on the geochemistry of exposed surface materials in Victoria Land, Antarctica, the MDV could be a potential material source area (PSA), but there are limitations to this approach. All of these studies note significant overlap of Sr and Nd isotopic measurements of Victoria Land samples among several local rock types or other Southern Hemisphere sources, and therefore they cannot absolutely discern the ultimate source(s) of the materials. While Delmonte et al. (2010b) examined sediments on natural landforms as aeolian material, only a few studies have investigated the chemistry of modern "in-situ" aeolian material (Deuerling et al., 2014; Diaz et al., 2018a; Šabacká et al., 2012). In other words, local PSAs need to be better constrained. This study offers the first analysis of a combination of mineralogy, major oxide, and trace element measurements for "in-situ" aeolian material from several locations in the MDV. The geochemistry of this material is compared to local lithologies and potential Southern Hemisphere sources to constrain the MDV as a contributor and sink of material transported to the Antarctic periphery and interior, and to investigate potential contributions of remote sources to the Antarctic aeolian system.

2. Study sites

We focus on four valleys within the MDV network, where mean annual valley floor temperatures range from −15 °C to −40 °C and annual precipitation is generally less than 5 cm water equivalent (Doran et al., 2002; Fountain et al., 2009). Our study site elevations range from ∼20 to 950 m.a.s.l., though the highest peaks in the region reach upwards of 3,000 m. The geology of the MDV is comprised of four main rock types: metamorphic basement complex (gneiss, marble, quartzite and schist) of Cambrian/Pre-Cambrian age, Beacon Supergroup strata (sandstone, shale and coal) of Devonian-Triassic age, Ferrar Dolerite of Jurassic age, and the McMurdo Volcanic Group of Cenozoic age (Kyle et al., 1979; McKelvey and Webb, 1962). In addition, the basement complex was intruded by granitic rocks comprising the Granite Harbor Intrusives in the Early Cambrian to Middle Ordovician, and these plutons are seen on valley walls throughout the region (Angino et al., 1962). The relative contributions of each of these major rock types, the tills produced from the rocks, and therefore the potential entrainable materials, vary throughout the region. The locations of the individual study sites are shown in Fig. 1.

2.1. Miers Valley

In Miers Valley (∼250 m.a.s.l.), the valley floor is predominately weathered granite with quartz and marble pebbles ubiquitous in the desert pavement (Clayton-Greene et al., 1988) and the surface is highly eroded and porous. The eastern end of the valley is dominated by marine volcanics from the Ross Sea Drift (Clayton-Greene et al., 1988). The surficial materials also contain lacustrine sediments comprised of calcite, gypsum, and aluminosilicate minerals (Clayton-Greene et al., 1988), which are remnants of a former proglacial lake, Glacial Lake Trowbridge (Stuiver et al., 1981). Much of this surficial material has carbonate coatings on the unexposed side, which likely developed during inundation of the valley (Clayton-Greene et al., 1988). The presence of basaltic material, such as kenyte (a porphyritic phonolite with anorthoclase, olivine, augite, and glass), indicates glacial drifts originating from the East, where the McMurdo Volcanic Group is present in abundance (Clayton-Greene et al., 1988).

2.2. Taylor Valley

The geology of Taylor Valley (∼20-70 m.a.s.l.) has been characterized in detail (e.g. Angino et al., 1962); therefore this description serves as a brief overview. The major rock types include the basement complex, granitic intrusives, dolerite, and a number of McMurdo Volcanic Cones. Beacon Sandstone outcrops are exposed to the west at higher elevations beyond the length of the valley itself. Kenyte from Mt. Erebus is present in the eastern portion of the valley, suggesting input from the WAIS as it progressed northward during glacial periods.

Taylor Valley contains three major basins: Lake Fryxell basin to the east, the centrally located Lake Hoare basin, and Lake Bonney basin to the west. Samples were collected in a transect from Explorer's Cove (∼70 m) to Lake Fryxell (F6) (∼20 m) and East Lake Bonney (∼70 m) (Fig. 1). The valley floor surface is characterized by mostly sandy gravel tills, exposed bedrock, and volcanic rocks, which have been reworked by the advance and retreat of both the East and West Antarctic Ice Sheets (Porter and Beget, 1981). Much of Taylor Valley was inundated during the LGM by Glacial Lake Washburn, which resulted in lacustrine deposits, such as calcium carbonate and aluminosilicate clays, scattered throughout the valley floor. These valley floor materials in Taylor and Miers Valleys have only been "exposed" since the late Pleistocene or early Holocene as the lakes declined in area (Stuiver et al., 1981).

2.3. Victoria Valley

The geology of Victoria Valley (∼450 m.a.s.l.) consists of complex folded metamorphic rocks, and sandstones that overlie dolerite sills (Gunn and Warren, 1962). Larger exposed rocks are comprised of white granular marbles, paragneisses, granulites, and quartzofeldspathic schists (Allen and Gibson, 1962). Victoria Valley contains extensive sand sheets and dunes throughout the valley floor along with various drifts originating from the east and north (Calkin and Rutford, 1974). Lacustrine algae and carbonate plate deposits are widespread, suggesting that, like the valleys to the south, portions of the Victoria Valley were inundated during the LGM (Hall et al., 2002), however much of the valley is believed to have been ice free since the Miocene (Bockheim and McLeod, 2013).

2.4. Alatna Valley

Compared to the other valleys described in this work, Alatna Valley (∼950 m.a.s.l.) is less studied, and there is little information describing its exposed surface. The landscape contains large-amplitude meltwater scours and likely achieved its present form in the warmer middle Miocene through the formation and movement of both rivers and glaciers (Sugden and Denton, 2004). This is evidenced by the preservation of unconsolidated deposits, presence of small Miocene volcanic cones (Wilch et al., 1993), and abundance of fjord sediments (Prentice et al., 1993). The valley floor is covered with glacial tills and roches moutonnées. Surrounding erosional surfaces have dolerite, granite, sandstone and orthoquartzite materials (Pocknall et al., 1994).

3. Methods

Aeolian materials were collected between 2013 and 2015 using Big Spring Number Eight (BSNE) isokinetic wind samplers (Fig. A.1) at six collection sites throughout the MDV (Fig. 1). Each BSNE trap contains 5 collection heights above the surface (5, 10, 20, 50, 100 cm), although relative elevation terms (bottom lower, bottom middle, bottom upper, middle, top) are used here to account for potential movement of the collection boxes by strong winds over the periods of deployment. Collection site elevations within each valley were determined post-collection using GPS coordinates and the Reference Elevation Model of Antarctica (REMA), released in 2018 by the Polar Geospatial Center (PGC). Recent advances in digital surface modeling (e.g. REMA) have provided higher resolution and more accurate elevation data than values presented in previous studies. In 2013 and 2014, collections were made twice: in November for winter material and in January for summer material. Samples were stored in clean Whirl-Pak Bags at −20 °C prior to sample analysis, and were later ground using a ceramic mortar and pestle after thawing to room temperature (∼20 °C). The mortar and pestle were cleaned between samples using dilute ethanol, then rinsed with DI water and dried.

3.1. Bulk geochemistry

Between 5 and 10 g of sediment from each sample were sent to SGS Canada Inc. in Lakefield, Canada for analysis of major oxides and a suite of 35 minor and trace elements. The samples were crushed to where 75% of the material could pass through a 2 mm sieve, then pulverized to where 85% passed through 75 microns. Major oxide analysis was conducted on sample beads, which were made through ore grade borate fusion and analyzed via X-ray fluorescence (XRF). Major and trace elements concentrations were determined through ICP-AES/ICP-MS analysis after sodium peroxide fusion. The whole rock XRF analysis required 3.0 g of material,

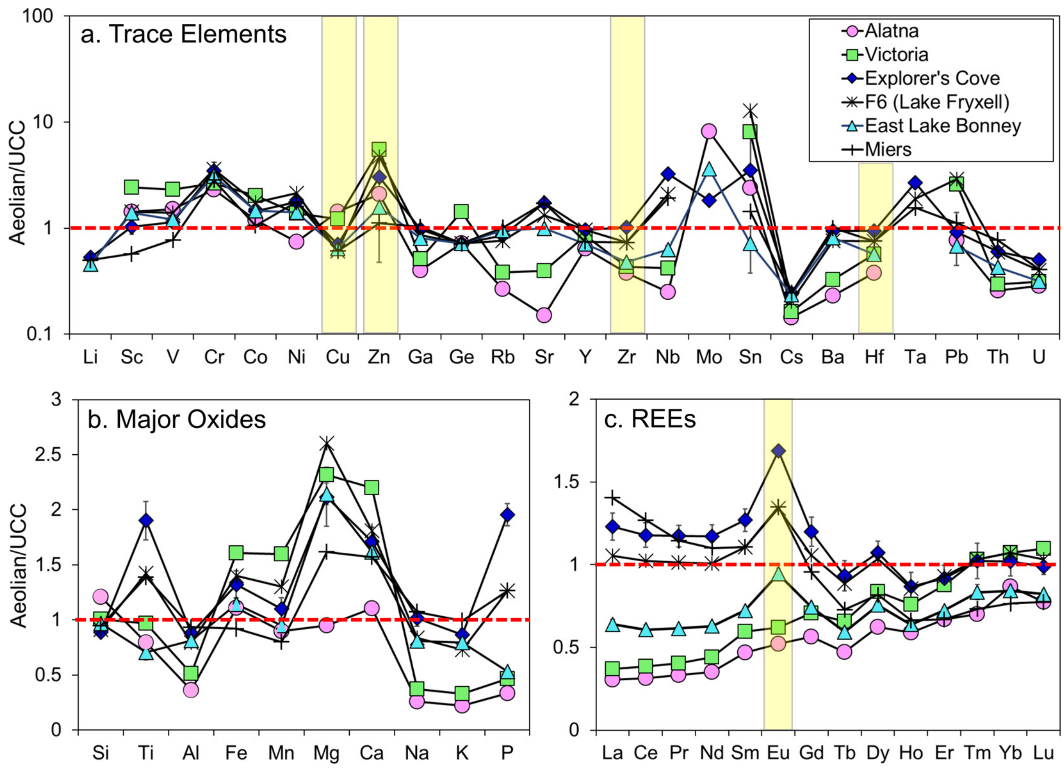

Fig. 2. Trace element (a), major oxide (b) and REE concentrations of aeolian materials normalized to the upper continental crust (Rudnick and Gao, 2003). All samples are the highest collection heights at each location. Explorer's Cove and East Lake Bonney are averaged values from full year and winter collections. The error bars represent the standard deviation. Colors correspond to sample locations in Fig. 1. Yellow band represent areas of particular interest with respect to sediment provenance. See Table A.2 for references. (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

whereas the suite of minor and trace elements required 0.2 g, therefore only some samples had sufficient mass (Table A.1) for the analysis. Although measurements of 35 trace element concentrations were attempted, all the samples were below the detection limit for Be, Ag, As, Bi, Cd, In, and W. Analytical detection limits and precision are listed in Appendix B.

3.2. X-Ray Diffraction (XRD)

XRD analyses were conducted at the Subsurface Energy Materials Characterization & Analysis Laboratory (SEMCAL), School of Earth Sciences, The Ohio State University. For the highest collection height samples (top or mid) from each location, approximately 2.5 g of sediment were hand ground in a mortar and pestle and front loaded into stainless steel sample holders. There was insufficient mass to analyze samples from Alatna and Miers Valleys (Table A.1). Samples were analyzed using a PANalytical X'pert Pro X-ray Diffractometer equipped with a high speed X'Celerator detector. Each sample was scanned from 4° to 70° 2θ at 45 kV, 40 mA with a step size of 0.020° 2θ and 20 s per step. Qualitative mineralogy was determined using the PANalytical HighScore Plus analytical platform and the ICDD PDF 4+ mineral database.

3.3. Scanning Electron Microscopy (SEM)

Electron microscopy was performed on samples from the upper-most collection heights (top or middle) from all sites using a FEI Quanta 250 Field Emission Gun (FEG) SEM equipped with a Bruker X-Flash X-ray spectrometer and Bruker Quantax software at SEMCAL. Parameters were set to an accelerating voltage of 15.00 keV and a working distance of 13.6 mm. Energy dispersive X-ray spectroscopy (EDXS), with an interaction volume for characteristic X-rays of approximately 1-3 μm, was used for elemental microanalysis of an aliquot of each sediment sample, with a focus on REEs and trace metals as inclusions, flakes and encrustations. Elemental maps were also generated to detail the incorporation of REE inclusions. These methods are similar to those described in Diaz et al. (2018a).

4. Results

4.1. Sediment geochemistry

Concentrations of major oxides and trace elements for all samples are presented (Appendix C) and compared to the chemistry of mean upper continental crust (UCC) values (Fig. 2). Bulk oxide composition ranged from 80.6% SiO_2 in Alatna Valley to 57.7% at F6. The higher elevation sites had greater SiO_2 values than lower elevation sites, while the lower elevation sites had higher P_2O_5, Al_2O_3 and K_2O values. Phosphate rich inclusions or surface crusts were also observed in SEM images in Taylor and Miers Valley samples (Fig. 3). The top-most sample from Victoria Valley had the highest concentrations of Fe_2O_3 and CaO at 8.71% and 8.12%, respectively, likely reflecting contributions from more mafic lithologies. The samples had different TiO_2 percentages based on location, with the higher elevation sites of Alatna Valley, Victoria Valley and East Lake Bonney having lower percentages compared to the lower elevation and coast sites of F6 and Explorer's Cove (Fig. 2). Compared to the other samples studied, the Alatna Valley sample is the most distinctive due to its high SiO_2 content and low Mg and Ca values.

Trace metal content of the aeolian samples differed among the four valleys, but most concentrations were within an order of magnitude of the average crustal abundance (Fig. 2). In particular, Cr, Zn, and Tn had relatively high enrichments, while U and Th were depleted. The lower elevation sites had slightly more U (~0.7 ppm) than the higher elevation sites. Ta and Nb were enriched in Taylor and Miers Valley samples (with the exception of East Lake Bonney),

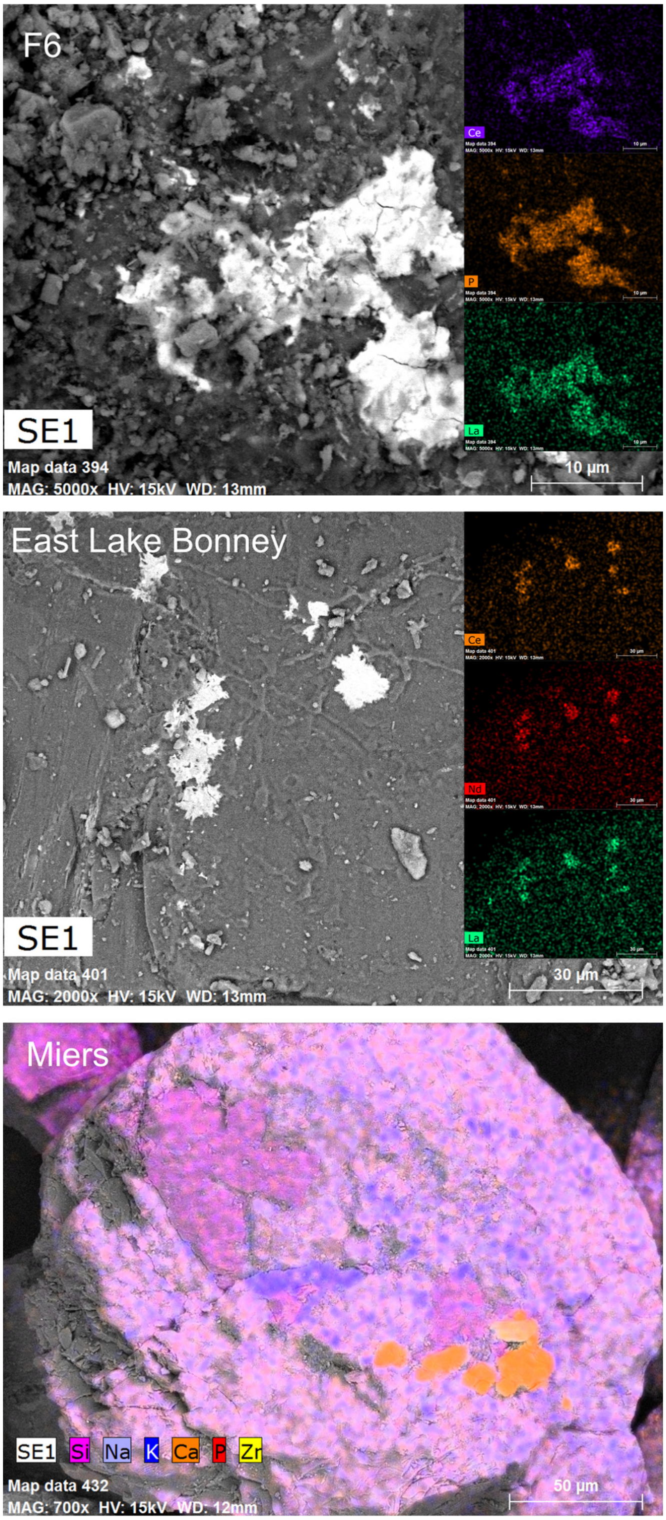

Fig. 3. SEM images of REE and trace element inclusions in Taylor and Miers Valley samples. Small colored images for F6 and East Lake Bonney depict specific element occurrence and distribution. An elemental map is shown for Miers with a P-rich zircon inclusion on a phyllosilicate.

while Ta was below the detection limit and Nb was depleted only in the higher elevation sampling locations, suggesting a more volcanic source in the lower elevation, higher latitude valleys (Hall et al., 1995). Alatna and Victoria Valleys were most depleted in U, Th, Zr and Hf, indicating a potential loss of zircons, and most strongly deviated from the lower elevation sites in their low Ga, Rb, Sr, Nb, and Ba concentrations (7-10 ppm, 25-32 ppm, 48-126 ppm, 3-6 ppm, and 144-205 ppm respectively) (Appendix C, Fig. 2). There were Zr inclusions in Taylor and Miers Valley samples (Fig. 3), which also had Zr concentrations most similar to UCC (Fig. 2).

Rare earth elements can be separated into light (Sc, La, Ce, Pr, Nd, Pm, Sm and Eu) and heavy (Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) fractions. The elements Sc and Y are grouped with the light and heavy REEs respectively due to similarities in ionic radius and geochemical behavior. The concentrations of light rare earth elements (LREEs) varied most greatly by location, where the higher elevation and more inland samples were depleted in LREE compared to lower elevation and coastal samples (Fig. 2). While all locations were similar in their heavy rare earth elements (HREE) concentrations, Taylor and Miers Valley samples had positive Eu anomalies, identified by large spikes in Eu concentrations relative to other REEs, while Victoria and Alatna Valleys did not. Eu can substitute for Ca in plagioclase; therefore, this relative enrichment likely indicates a more plagioclase-rich source in Taylor and Miers Valleys. Mineral phases bearing REE (La and Ce) were observed in SEM images (Fig. 3).

4.2. Mineralogy

X-ray diffraction maxima were sharp and symmetrical, suggesting well-defined crystalline mineral phases in all samples, and a limited abundance of clays and poorly crystalline oxyhydroxide phases (Fig. 4). Additionally, no clay peaks were observed in the 59-61° 2θ range. Previous work has demonstrated low concentrations of clay minerals in stream sediments and surface soils in Taylor Valley (Dowling et al., 2019). Quartz, a suite of feldspars with varying compositions, pyroxenes, micas, and amphiboles were observed in all samples. There were multiple pyroxenes present within individual samples, mainly calcium, magnesium and iron pyroxenes, with d-spacings (and therefore chemical compositions) that are consistent with either pigeonite, augite, or hedenbergite (Fig. 4). Many of the minerals observed commonly occur in anorthosite, basalt, andesite, kenyte, and dolerite, rocks previously identified within the MDV region (Calkin and Rutford, 1974; Kyle et al., 1990). While the mineralogy was similar among many of the sites, there also were distinct differences. For example, Victoria Valley had the more ordered microcline, common in granites, instead of sanidine, which was identified in Taylor and Miers Valley samples (Fig. 4). Mica was not detected in the Victoria Valley sample (no discernable 10 Å peak), consistent with low K and Na bulk composition (Fig. 2b). There are strong diopside peaks (35-36° 2θ range) and serpentine in the Taylor Valley samples (Fig. 4), suggesting a mafic or ultramafic igneous source.

5. Discussion

Previous studies have successfully used major oxide geochemical variation diagrams (Ferrat et al., 2011; Moreno et al., 2006), isotopic measurements (Delmonte et al., 2010a; Deuerling et al., 2014; Winton et al., 2016), and REE signatures (Muhs et al., 2010; Wegner et al., 2012; Wei et al., 2017) to examine the provenance and geologic sources of aeolian material and thereby infer sources and pathways of dust transport. We have used a combination of these geochemical tools here to investigate the source of aeolian material in the MDV.

5.1. Delineation of major oxide chemistry

The major oxide geochemistry of aeolian samples was compared to the geochemistry of McMurdo Volcanics, Ferrar Dolerite, granitoids from the MDV, and Beacon Sandstone (Table A.2), with respect to SiO_2 and $Na_2O + K_2O$ (Fig. 5). All the aeolian samples

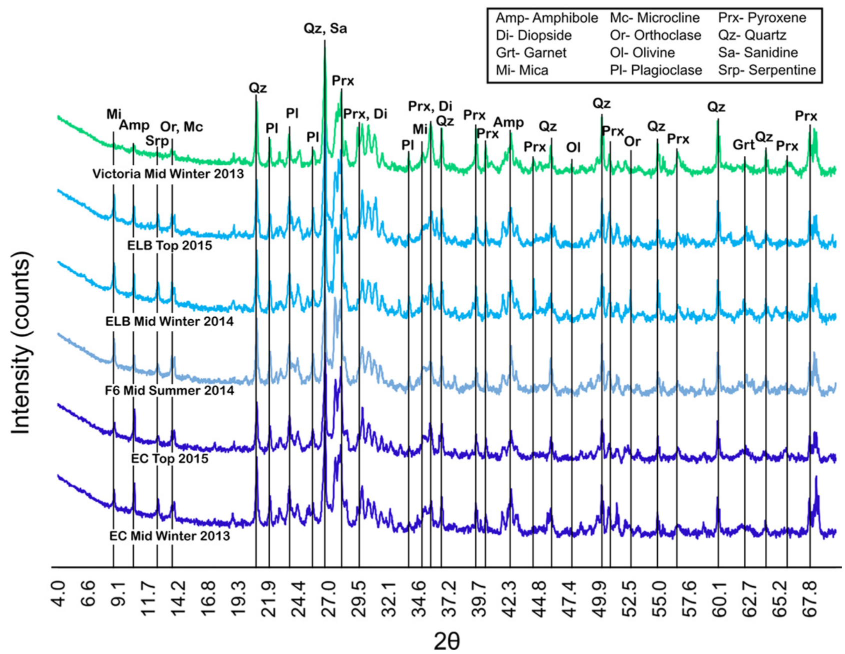

Fig. 4. X-ray diffraction scans for the upper most samples of MDV aeolian material. Different seasons are plotted for Explorer's Cove (EC) and East Lake Bonney (ELB). The metric on the x-axis is 2θ, which was used to determine mineralogy. The vertical black lines correspond to peaks attributed to certain minerals and the relative intensities can be compared to estimate mineral abundance.

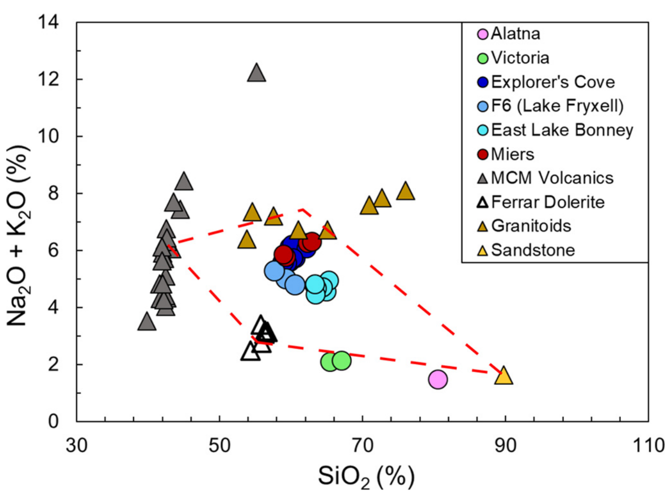

Fig. 5. Major oxide data of aeolian material and potential source rocks. Red dashed lines represent potential mixing of source material, where the chemistry of any samples that fall on between the lines can be explained by a mixture McMurdo Volcanics (Cooper et al., 2007), Ferrar Dolerite (Antonini et al., 1999), granitoids (Smillie, 1992), and sandstone (Roser and Pyne, 1989). See Table A.2 for references.

had higher percentages of SiO_2 than McMurdo Volcanics and Ferrar Dolerite, which suggests another component- either SiO_2 material from the Beacon Supergroup, or material from the lower elevation, more felsic crystalline basement rocks. Samples from Explorer's Cove and Miers Valley have major oxide chemistries most similar to nearby granitoids (Fig. 5), while lower percentages of Na_2O + K_2O in Victoria and Alatna Valleys suggest a different source, potentially quartzite, which is also supported by the mineralogy data (Fig. 4).

Potential mixing lines were drawn between possible source materials (Fig. 5), where the chemistry of any sample that falls on or between the lines can be explained by a mixture of these four rock types. All samples from Taylor and Miers Valleys fall between the rock mixing lines, suggesting a sediment composition that is a potential mixture of all four rock types and affirms the idea that the Beacon Sandstone and possibly the crystalline basement rocks are contributing to the aeolian composition in these locations. The sandstone is exposed at higher elevations and could potentially represent a source of dust, especially due to the flow of strong foehn winds from the TAM into these valleys to the east (Šabacká et al., 2012). Alatna and Victoria Valleys fall just outside of the mixing lines (Fig. 5). These data suggest that either an additional, unknown source of material exists at these high elevation sites, or there are regional compositional variations in the rocks that our simple conceptual model has not considered.

PSAs identified by Baccolo et al. (2018) were compared to the Al, Ca, Na, and K (A-CN-K) composition of aeolian material from this study (Fig. 6; Table A.2). While significant overlap of PSAs makes identifying singular sources using this method difficult, general contributions can be suggested. Victoria and Alatna Valley samples plotted elongated on the Al_2O_3-CaO + Na_2O axis suggesting early phases of alteration and weathering. The lower elevation Taylor and Miers Valley samples had relatively more K_2O, likely from K-feldspar or its K-rich weathering products (Fig. 4), which was observed in the XRD data with relatively higher intensity K-feldspar reflections (Fig. 3). MDV aeolian samples appear most similar to a mixture of the MCM Volcanics, Ferrar Dolerite and granite. Interestingly, Victoria Valley has a bulk oxide chemistry most similar to volcanic rocks and Patagonian dust (Fig. 4). The volcanic contribution appears large compared to the other locations and could represent another unknown mixture of materials not seen elsewhere. However, the mineralogy and trace element data for the Victoria Valley samples imply a more metamorphic source due to the wide compositional array of feldspars and amphiboles, common in granite and gneiss (Fig. 4). This is consistent with previous work that characterized granites and gneiss from the Granite Harbor Intrusive complex (Allen and Gibson, 1962; Gunn and Warren, 1962).

5.2. Geographic provenance

Strontium and neodymium isotopic concentrations are generally expressed as a set of ratios, specifically $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$,

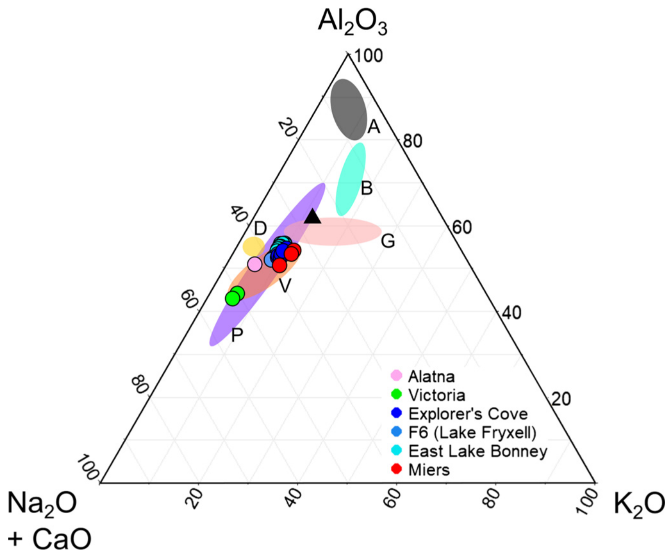

Fig. 6. A-CN-K ternary diagram of MDV aeolian material compared to potential local source rocks and Australia (A, grey) (Mclennan et al., 1983) and Patagonia (P, purple) (Gaiero et al., 2007). Source rocks include McMurdo Volcanics (V, orange) (Cooper et al., 2007), Ferrar Dolerite (D, yellow) (Antonini et al., 1999), granitoids (G, pink) (Smillie, 1992), and sandstone (B, teal) (Roser and Pyne, 1989). The black triangle represents the chemistry of the upper continental crust (Rudnick and Gao, 2003). See Table A.2 for references.

where $^{143}Nd/^{144}Nd$ is typically expressed normalized to the chondrite value as εNd. These isotopes fractionate based on crust-mantle differentiation age, the cycling of crustal materials and weathering, and therefore vary based on region.

Aeolian material on Taylor Glacier had a $\mathcal{E}$Nd and $^{87}Sr/^{86}Sr$ signature that was most similar to local MDV rocks listed previously, but isotopic signatures of the material from the central and coastal locations in Taylor Valley also overlap with South American and New Zealand source signatures (Aarons et al., 2019 and references within). Recent work on southern high-latitude dust transport found that aeolian transport of material from Patagonia and New Zealand to Antarctica is possible, where >8% of trajectories reach Antarctica after 8 days (Neff and Bertler, 2015). Trajectories from Australia are less efficient with ~2% arriving in Antarctica after 10 days. This modeling work suggests that materials from other, more remote, Southern Hemisphere sources could potentially contribute to modern Antarctic dust. However, these isotopic overlaps lead to non-unique conclusions using this tool alone to discern sediment provenance in Antarctica.

Similar to isotopic ratios, REE ratios can help determine the mineral/rock types present and thus can be used to compare and contrast geologic materials, and determine the nature of the source location (Ferrat et al., 2011; Wei et al., 2017). REEs have low solubilities and remain primarily in the solid phase during transport, therefore maintaining the REE signature of the original source material (Piper and Bau, 2013). Therefore, light and heavy rare earth element ratios (L/HREE) can generally be used to identify various minerals, as it is assumed that no major alteration of material has occurred. The degree of alteration (i.e. chemical weathering) can be determined by calculating chemical index of alteration (CIA) values, which are generally low (<60%) and suggest primary mineral occurrence with little to no chemical alteration for McMurdo Dry Valley materials (Diaz et al., 2018b). This is consistent with the XRD data, which showed a high degree of crystallinity, and SEM observations. Additionally, La/Yb ratios normalized to the upper continental crust, $(La/Yb)_N$, can indicate the enrichment of the lightest over heaviest REEs. $(La/Sm)_N$ represents the differential enrichment of LREEs, while $(Gd/Yb)_N$ ratios indicate the degree of relative depletion of HREEs (Bhatia, 1985). $(Eu/Eu^*)_N$ indicates the degree of REE fractionation since Eu*, calculated by Equation (1), represents the interpolated Eu concentrations with no enrichment or depletion (Bhatia, 1985).

$$Eu/Eu^* = \left(Eu_N/(Sm_N * Gd_N)^{1/2}\right) \quad (1)$$

Eu/Eu*, La/Yb, La/Sm, Gd/Yb, and L/HREE ratios from the MDV aeolian sediments were compared to published values of McMurdo Volcanics, Ferrar Dolerite, granites and granitoids of the Granite Harbor Intrusive Complex, soil from Australia, soil and aeolian dust from Patagonia, dust from New Zealand, and Taylor Valley stream sediments (Fig. 7; Table A.2). Dust values from Patagonia, New Zealand and Australia were included because, as discussed previously, wind trajectories from these locations indicate that fine-grained material from these regions can potentially reach Antarctica (Li et al., 2008; Neff and Bertler, 2015).

REE ratio values were calculated in order to discern the source of material for our MDV aeolian samples. The ratios varied based on elevation and proximity to the coast (Fig. 7). Victoria and Alatna Valley samples were more enriched in the heaviest REE (Yb) (as evident from the lowest La/Yb ratios) and had the lowest Eu/Eu* ratio (Fig. 7). Low Eu/Eu* values and higher HREE content indicate lower feldspar abundance and a more mafic or less crustal source (see section 4.1). Explorer's Cove, F6, and Miers Valley all clustered with a relatively higher concentration of LREEs and a greater Eu/Eu* signature, suggesting a more felsic or crustal source. East Lake Bonney plots between these two end members and was most similar to dust (and therefore likely top soil) from Patagonia (Fig. 7). Alatna and Victoria Valleys were the most similar to each other and some of the Australian values. With the exception of the ~100 cm elevation sample, Miers Valley was the most similar to F6. Aeolian sediment in the MDV differs from local stream sediments within local basins. Stream sediments from the Bonney Basin were most similar to aeolian material at F6, while stream sediments from the Fryxell Basin were most similar to aeolian material at Explorer's Cove. This supports findings from Diaz et al. (2018a) who suggested a down-valley transport of material in Taylor Valley, probably by strong foehn winds, towards the coast.

Potential mixing lines were drawn between the local rock values, where the REE chemistry of any samples that plot on or between the lines can be explained by a mixture of MCM Volcanics, Ferrar Dolerite, and/or granites. Most samples from Taylor and Miers Valleys plotted within the mixing lines for all REE ratios, except for East Lake Bonney. Samples from Alatna and Victoria Valleys plotted slightly outside the mixing areas for all ratios (Fig. 7). A mixing model mathematically representing the relative contributions of each MDV rock type is described in Appendix D. No combination of Ferrar Dolerite, MDV Volcanics, or granite can explain the geochemistry of Alatna and Victoria Valley samples, regardless of REE ratio. These data provide support for either a distant source of material not represented in the MDV lithology, an unidentified local source (potentially of variable igneous composition), or the alteration of primary materials at these high elevations.

5.3. A case for long-traveled material

In addition to the wind trajectory models previously discussed (i.e. Li et al., 2008; Neff and Bertler, 2015), there is geochemical and biological evidence supporting long-range transport of materials to Antarctica in the past. Dissolved black carbon with a woody chemical signature was identified in ancient brines at the bottoms of lakes in the MDV (Khan et al., 2016). Due to a lack of current wooded vegetation and no forest fire history in Antarctica, this black carbon must have originated from another Southern Hemi-

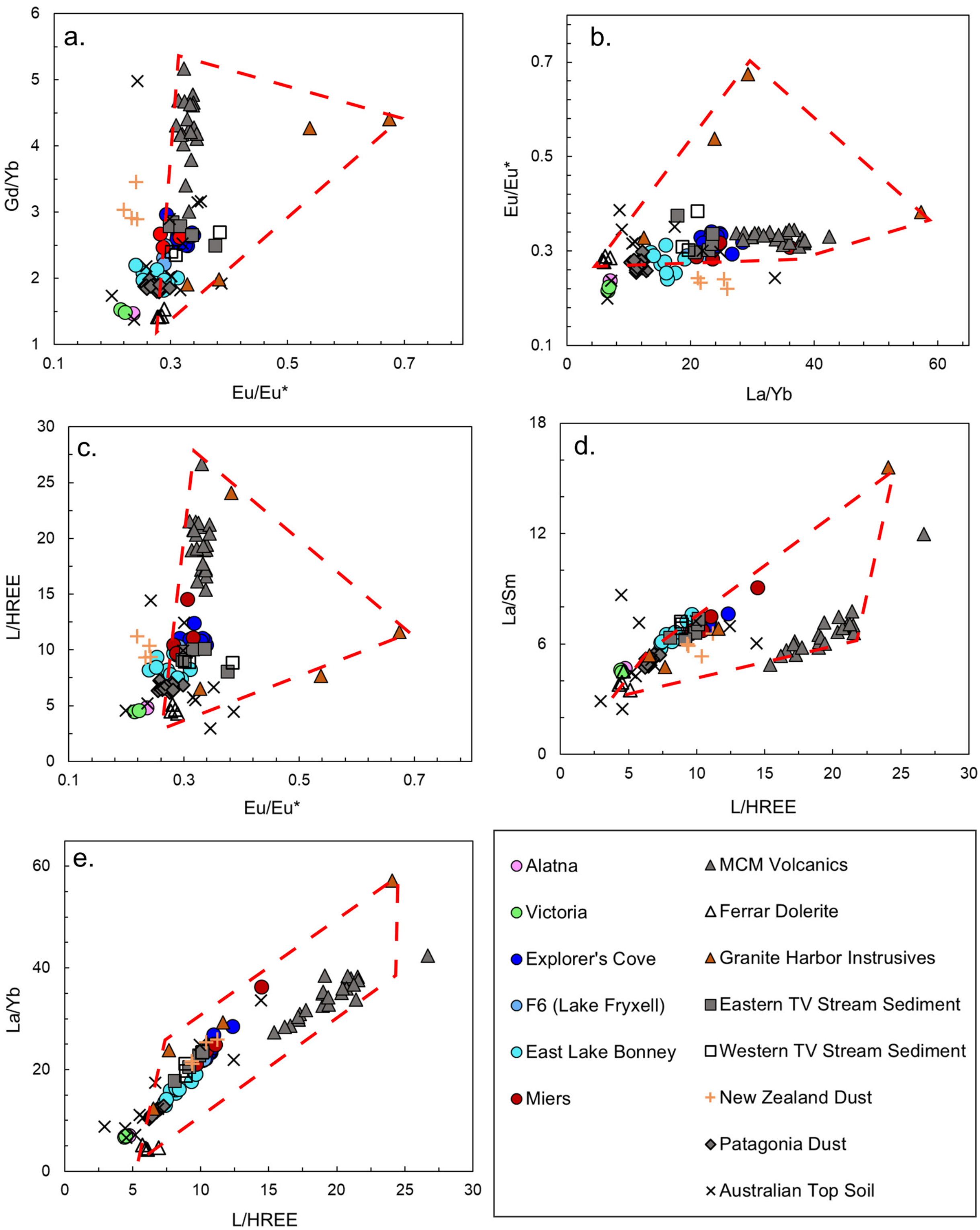

Fig. 7. REE ratios calculated from all MDV aeolian material and compared to published signatures from potential source rocks [McMurdo Volcanics (Cooper et al., 2007); Ferrar Dolerite (Antonini et al., 1999); Granite Harbor Intrusive Complex (Martin et al., 2015)], foreign dust [Australian soil (Diatloff et al., 1996; Martin and McCulloch, 1999; Mclennan et al., 1983); Patagonian dust (Gaiero et al., 2003, 2004); New Zealand dust (Marx et al., 2005)], and stream sediments (Dowling et al., 2019). All values were normalized to the average upper continental crust (Rudnick and Gao, 2003). Red dashed lines represent potential mixing of source material, where the chemistry of any samples that fall on between the lines can be explained by a mixture of source rocks. See Table A.2 for references.

sphere source, potentially Patagonia (Markgraf and Huber, 2010). Volcanic ash from the Oruanui supereruption in New Zealand (∼25 kya) was found in a West Antarctica ice core. Simulations of this eruption suggest that the volcanic material should be found in much of East Antarctica (Dunbar et al., 2017). Lastly, studies on the molecular genetics and phylogeny of microbial organisms near Mt. Erebus and the MDV suggest that some organisms are not endemic, but instead cosmopolitan, likely originating from South America and transported to Antarctica by winds (Archer et al., 2019; Herbold et al., 2014).

It appears that aeolian material in the MDV is primarily a mixture of local sediments and re-suspended material that has been previously deposited (Fig. 1). Additionally, our data suggest that long-traveled material could contribute to local dust signatures for inland and high elevation locations. Some material could originate from nunataks further south or inland on the Polar Plateau, however erosion and deflation from these features are unlikely to transport enough material to alter MDV dust chemistry. Mt. Erebus is another potential source. Undisturbed volcanic ash layers have been identified in high elevation (>1000 m.a.s.l.), hyper-arid environments in the MDV (Marchant et al., 1996) and glass from Mt. Erebus has been identified in McMurdo Sound, but there is only rare or trace abundance along the northern McMurdo Dry Valley coast (Chewings et al., 2014). These volcanic materials are likely transported further north into the Southern Ocean, deposited further inland in the MDV, and/or remain suspended throughout Victoria Land. Volcanic end-members from the Erebus province were included our geochemical analyses (Figs. 5–7; Table A.2), but do not appear to be a major material source in Alatna and Victoria Valleys based on their REE ratio values (Fig. 7).

Taylor and Miers Valleys, with the possible exception of East Lake Bonney, are dominated by local sources (Deuerling et al., 2014; Diaz et al., 2018a). While Lake Bonney is not considered a high elevation location, strong winds originating from the higher elevation polar plateau and moving into Taylor Valley towards the coast are potentially transporting and depositing material from higher elevations beyond the Bonney basin. Since Lake Fryxell and Explorer's Cove are at the eastern, coastal end of the valley where foehn winds have the longest fetch over ice-free areas (Fig. 1), local resuspended material likely overprints any other potential dust signals from modern fallout and accumulation, if they exist in this region. In the MDV, mountain peaks and other high elevation features are important sources of material for local, lower elevation surfaces, and this is reflected by the similarity in REE chemistry between Taylor and Miers Valley aeolian materials and local rock types (Fig. 7).

The chemistry of Alatna and Victoria Valley samples cannot be explained solely by the geochemistry of the known local sediment sources investigated in this work. The long-range transport of aeolian materials is dependent on particle size and particle fallout rates. "Background dust", which in our context represents potential materials transported from Australia and Patagonia, is fine-grained (typically <5 μm) and fallout rates at Talos Dome north of the MDV ranged from 0.70 $mg\,m^{-2}\,yr^{-1}$ during the late Holocene to 7.24 $mg\,m^{-2}\,yr^{-1}$ during the LGM (Albani et al., 2012). Our sample masses were too low for quantitative grain-size analysis without the risk of contamination (Table A.1). However, data from previous work indicates that at ∼1 m above the surface, the eastern portion of Victoria Valley has a smaller grain size (mean of 150 μm) than Taylor Valley (mean of 450 μm) (Gillies et al., 2013). Additionally, in McMurdo Sound, Winton et al. (2014) show that between 10 and 50% of sediment on sea ice is <10 μm in diameter. The grain size in Alatna Valley is probably smaller than Victoria Valley due its higher elevation and absence of large sand dunes.

Though much of Taylor and Miers Valleys were inundated during the LGM (Clayton-Greene et al., 1988; Stuiver et al., 1981), Alatna and Victoria Valleys have been ice-free for possibly >5 Myr (Bockheim and McLeod, 2013; Denton and Sugden, 2005). The modern background dust fallout rate in the MDV is too low to overprint the aeolian material signal from (re)suspended local surface materials. However, we argue that the surface ages of Alatna and Victoria Valleys are sufficient to have accumulated considerable amounts of long-traveled dust. If we perform a simplified calculation assuming an average fallout rate for glacial and interglacial periods of 3.97 $mg\,m^{-2}\,yr^{-1}$ (Albani et al., 2012) over the last 5 Myr, Alatna and Victoria Valleys could have accumulated ∼20 $kg\,m^{-2}$ of background dust. This material is likely re-suspended along with material derived from local weathering, and influences the geochemical signature, possibly explaining the deviations from local sources in Figs. 5 and 7.

Locations at higher elevations (e.g. Alatna and Victoria Valleys) may be accumulating long-traveled dust from Australia and Patagonia, and to a lesser extent, New Zealand (Li et al., 2008; Marx et al., 2018; Neff and Bertler, 2015). Patagonia was a major source of aeolian material during glacial periods at Taylor Dome (Aarons et al., 2019; Gabrielli et al., 2010), yet we do not find overwhelming evidence of South American dust provenance based on the REE ratio values, and there is significant overlap in potential sources based on the bulk oxide composition (Figs. 6 and 7). Instead, Australia appears to be an important source. Previous studies have identified Australian dust in East Antarctic ice cores. During interglacial and drought periods in Australia, this dust may be dominant compared to dust from Patagonia (De Deckker et al., 2010; Revel-Rolland et al., 2006).

Relative abundances of trace elements can also be key indicators of long-traveled materials. Zr and Hf are preferentially removed during dust transport due to gravitational sorting of zircons. Compared to the UCC, these elements were the most depleted in our highest elevation samples (Fig. 2), which may suggest a long-traveled material source to this region (Marx et al., 2005). Zircons can also be rich in REEs, which might explain why REEs normalized to the UCC are lower for the samples that are suspected to have accumulated this long-traveled dust (Fig. 2). Though Zr and Hf are common in mafic and ultramafic lithologies, which were identified in all samples by XRD (Fig. 4), their depletions are not likely solely from regional surface compositional difference, but instead may also reflect a longer-traveled source.

Similarly, enrichments of Cu and Zn measured in the Vostok ice core were highest during glacial periods and were determined to be from a terrestrial source, likely from Patagonia or Australia (Hong et al., 2004), further supporting our case for long-traveled dust. We observed relative enrichments of Zn in all samples, but only Cu enrichment in the Alatna and Victoria Valley samples (Fig. 2a). Explorer's Cove and F6 materials are likely enriched in Zn due to their proximity to McMurdo Station, high helicopter traffic in this region, and proximity to Mt. Erebus (Lyons et al., 2018; Zreda-Gostynska et al., 1997). Though Alatna and Victoria Valleys are geographically isolated and are not frequented by helicopters and other aircraft, it is possible that anthropogenic activity in the Ross Sea region since the 1960s has resulted in pollution researching these locations. SEM images of Alatna and Victoria Valleys show flakes of Zn, Sn, Pb and Bi on aeolian grains, possibly anthropogenic in origin, though it is unclear whether these particles adhered locally or during long-range transport.

While volcanoes are a source of metals to the atmosphere, concentrations of Zn and Cu in Mt. Erebus plumes are 1-2 orders of magnitude lower than concentrations of aeolian materials collected in Alatna and Victoria Valleys (Zreda-Gostynska et al., 1997). Long-term accumulation of these materials in Alatna and Victoria Valleys could explain the enriched Cu and Zn values, however, if this was truly the dominant source, we would have expected Cd, V, and As enrichments as well (Appendix C). Considering our current knowledge of the geochemistry of MDV rock sources and Patagonian and Australian dust, it is likely that the geochemical "fingerprint" of aeolian materials from Alatna and Victoria Valleys includes the re-suspension of previously accumulated long-traveled dust. (Fig. 8).

6. Conclusions

Determining influence of aeolian material on modern and paleoclimate systems requires a greater understanding of the sediment

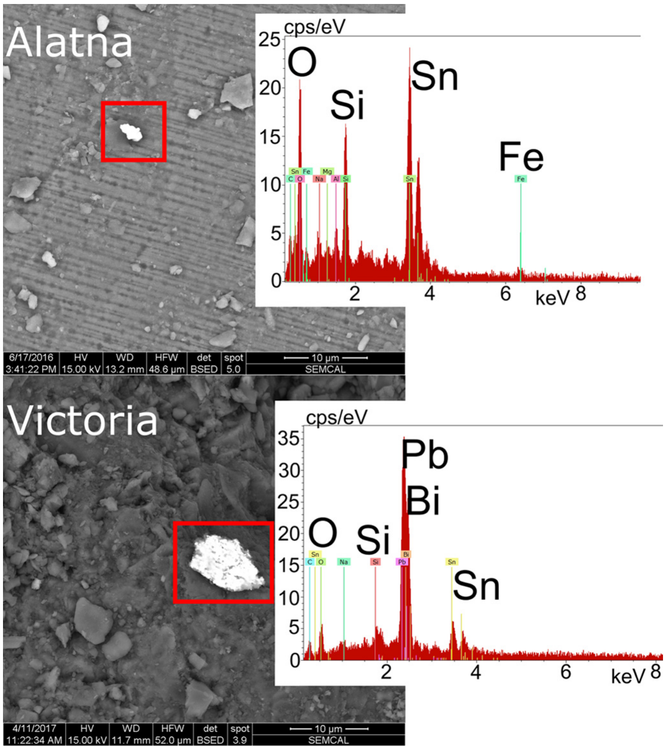

Fig. 8. SEM images of Victoria and Alatna Valley top-most samples. Red boxes indicate flakes on aeolian grain surfaces. Microanalysis was performed on the flakes and the EDXS spectra are inset images. Alatna depicts a Sn flake on a pyroxene grain while Victoria depicts a flake with Pb, Bi, and Sn composition over a Na rich silicate.

provenance. In the Southern Hemisphere, dust sources are generally limited to Patagonia, Australia, New Zealand, South Africa, and Antarctica. Numerous approaches have been developed to analyze and interpret potential source areas for dust contained in Antarctic ice cores. While these previous studies have carefully scrutinized geochemical data to identify and quantify Patagonian and Australian dust contributions during glacial periods, local source areas are still underrepresented.

Using a combination of mineralogical and bulk geochemical approaches, the geochemistry of modern aeolian material from the McMurdo Dry Valleys has been characterized. The mineralogy of MDV aeolian material generally reflects the broad geology of the region, with quartz, micas, amphiboles, and several different pyroxenes and feldspars likely from erosion of local volcanic, granitic, sandstone, and doleritic rocks, or glacial deposits derived from them. Trace element, major oxide, and rare earth element data show that low elevation sites in Taylor and Miers Valleys likely have aeolian material that is local in origin, while East Lake Bonney, and Alatna and Victoria Valleys are more complex.

At these high elevation and inland locations, the aeolian material geochemistry suggests other sources, perhaps longer transported ones that have accumulated since the Miocene, are important. The provenance geochemistry at these sites cannot be explained solely by the present knowledge of Dry Valley rock sources. While there was very little material collected such that extensive grain size analysis could not be undertaken in this study, future work should consider the potential differences in material source and geochemistry related to particle size. In addition, more complete analyses of rocks and potential local to regional dust sources are needed. These data would help constrain local sources of aeolian material to Antarctic inland and periphery regions, and aid in current and future investigations on the Antarctic climate cycles to better understand sediment provenance.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix. Supplementary material

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.epsl.2020.116460.

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