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Biogeochemical weathering of soil apatite grains in the McMurdo Dry Valleys, Antarctica

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ABSTRACT

The biogeochemical weathering of the mineral apatite links the lithosphere to the biosphere by releasing the essential nutrient phosphorus (P) into the soil ecosystem. In Taylor Valley, Antarctica, faster rates of apatite weathering may be responsible for the higher concentrations of bioavailable soil P that exist in the Fryxell Basin as compared to the Bonney Basin. In this study, we use scanning electron microscopy to quantify the morphology and surface etching of individual apatite grains to determine whether the degree of apatite weathering differs between the Fryxell and Bonney Basins as well as saturated and dry soil sediments. We show that apatite grains from the Fryxell Basin are rounder, have fewer intact crystal faces, and are more chemically etched than grains from the Bonney Basin. In the Bonney Basin, apatite grains from dry soils show few signs of chemical dissolution, suggesting that soil moisture is a stronger control on the rate of apatite weathering in the Bonney Basin than in the Fryxell Basin. In addition, etch-pit morphologies in the Bonney Basin are more clearly controlled by the hexagonal crystal structure of apatite, while in the Fryxell Basin, etch pits demonstrate a wide range of morphologies without clear crystallographic control. Higher rates of apatite weathering in the Fryxell Basin may be due to the legacy of the physical abrasion of apatite grains during transport by a warm-based ice sheet, as well as the higher levels of precipitation and soil moisture closer to the coast. Our grain-scale approach provides a new perspective on P cycling in the McMurdo Dry Valleys and has implications for apatite weathering and P dynamics in the early stages of soil development.

1. Introduction

The availability of soil phosphorus (P) is an important link between the lithosphere and the biosphere. Unlike nitrogen, which has a large atmospheric pool that can be biologically fixed by microorganisms, P enters the biosphere through the biogeochemical weathering of P-bearing minerals. In young landscapes, most soil P is locked in mineral form and inaccessible to organisms (Walker and Syers, 1976). Over time, as P-bearing minerals weather, total soil P content decreases and the recycling of organic matter replaces mineral weathering as the dominant process in the soil P cycle (Walker and Syers, 1976). The progression from mineral to organic P has been noted across many chronosequences, and the rate of this trajectory is thought to be controlled by both parent material and climate (e.g. Filippelli and Souch, 1999; Cross and Schlesinger, 2001; Porder and Hilley, 2011; Mage and Porder, 2013). While a common approach to understanding soil P transformations has been to characterize P availability across a range of soil types and ages (e.g. Cross and Schlesinger, 1995; Yang and Post, 2011), we take a different approach by considering the grain-scale biogeochemical processes releasing P into the ecosystem.

A range of physical, chemical, and biological weathering processes control the release of bioavailable P from the lithosphere into the soil ecosystem. Apatite ($Ca_5(PO_4)_3(F,Cl,OH)$) is the most common P-bearing mineral group and is found in most igneous, metamorphic, and sedimentary rock types. Because apatite is a relatively soft mineral (Moh's hardness: 5), it has been suggested that the physical weathering of apatite grains could precondition them for biogeochemical weathering (Foellmi et al., 2009). Chemically, apatite is relatively insoluble at a near-neutral pH, but both solubility and dissolution rate increase rapidly with increasing acidity (e.g. Dorozhkin, 1995; Welch et al., 2002; Harouiya et al., 2007; Dorozhkin, 2012). The rate of apatite dissolution has been shown to depend on apatite composition (fluorapatite is less soluble than other apatites), the total reactive mineral surface area, and the supply and chemistry of weathering solutions (Foellmi et al., 2009;

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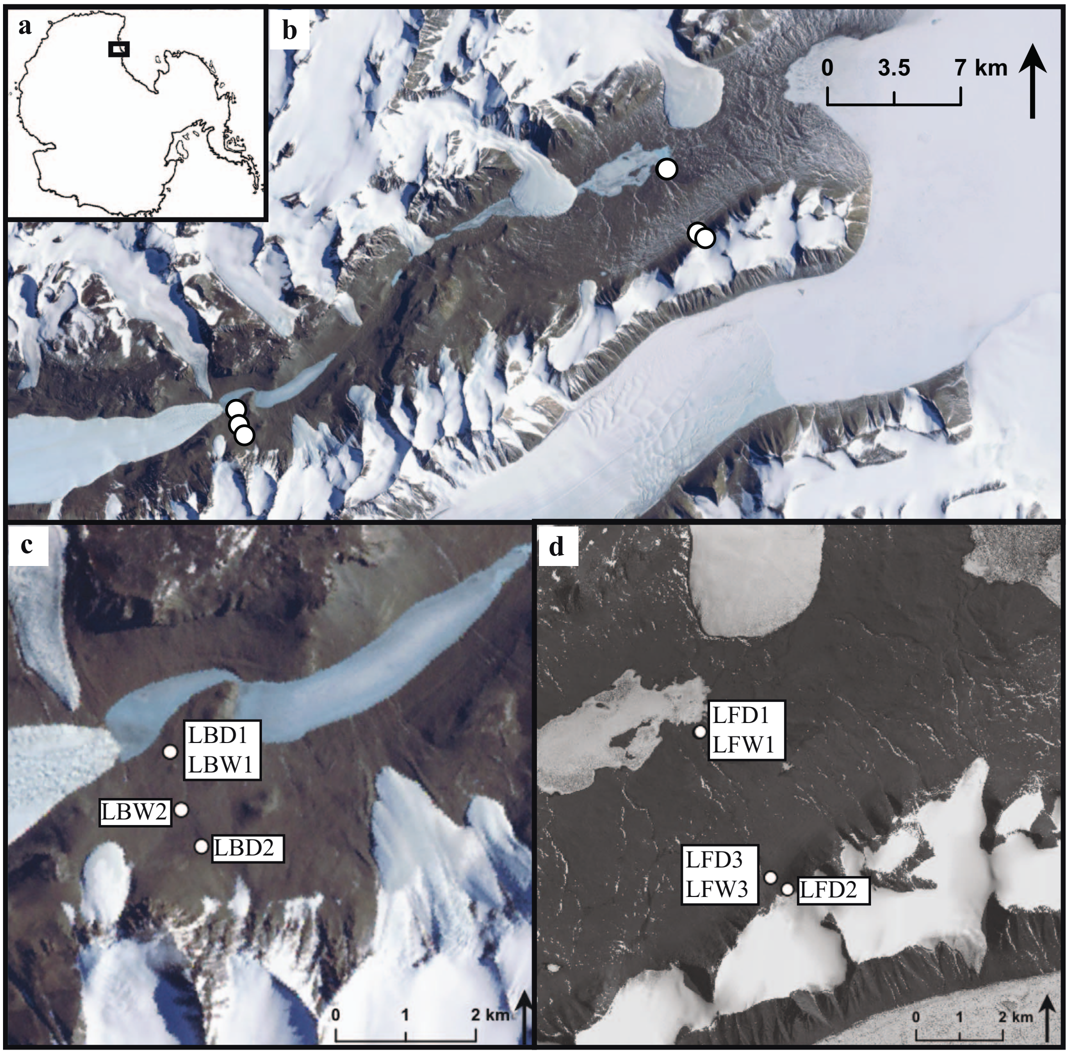

Fig. 1. Maps showing the location of the McMurdo Dry Valleys on the Antarctic continent (a), the sample locations in Taylor Valley (b), and close-ups of sample locations in the Bonney Basin (c) and the Fryxell Basin (d).

Table 1
Sample details. Samples are grouped by basin and then ordered by elevation.

Sample ID	Basin	Latitude	Longitude	Elevation (masl)	Moisture	# of grains analyzed
LBD1	Bonney	−77.72507	162.31468	111.62	Dry	49
LBW1	Bonney	−77.72507	162.31468	111.62	Saturated	66
LBW2	Bonney	−77.73242	162.32173	248.79	Saturated	87
LBD2	Bonney	−77.73709	162.33408	350.01	Dry	63
LFD1	Fryxell	−77.60946	163.25285	25.29	Dry	68
LFW1	Fryxell	−77.60929	163.25441	28.65	Saturated	67
LFD3	Fryxell	−77.63911	163.32462	227.36	Dry	82
LFW3	Fryxell	−77.63911	163.32462	227.36	Saturated	68
LFD2	Fryxell	−77.64145	163.34129	398.50	Dry	53

Wei et al., 2013). Finally, the rate of apatite dissolution can be dramatically enhanced by organic acids produced by microorganisms (Welch et al., 2002). Understanding the interactions among physical, chemical, and biological weathering of apatite is thus critical to determining how bioavailable P is released into the soil ecosystem.

The McMurdo Dry Valleys (MDVs) of Antarctica provide an opportunity to study the biogeochemical weathering of apatite in an ecosystem where the biosphere is clearly linked to geophysical conditions (Fountain et al., 1999). In the dry, basic, and nutrient-poor soils of the MDVs (Claridge and Campbell, 1977; Burkins et al., 2001), 60 to 90% of total soil P is in mineral form (Bate et al., 2007; Heindel et al., 2017). This suggests that MDVs soils remain in the early stages of soil P transformations, where the availability of soil P is tightly coupled to the weathering of primary apatite (Heindel et al., 2017). The natural variation in soil phosphorus content found within the MDV region has been linked to similar variations in the phosphorus content of aquatic ecosystem components, suggesting that soils have important downstream impacts on P concentrations and N:P ratios (Welch et al., 2010). In Taylor Valley, the focus of this study, the soils, streams, and lake water within the Bonney Basin are poorer in all forms of P than the Fryxell Basin (Priscu, 1995; Blecker et al., 2006; Bate et al., 2007; Welch et al., 2010; Heindel et al., 2017).

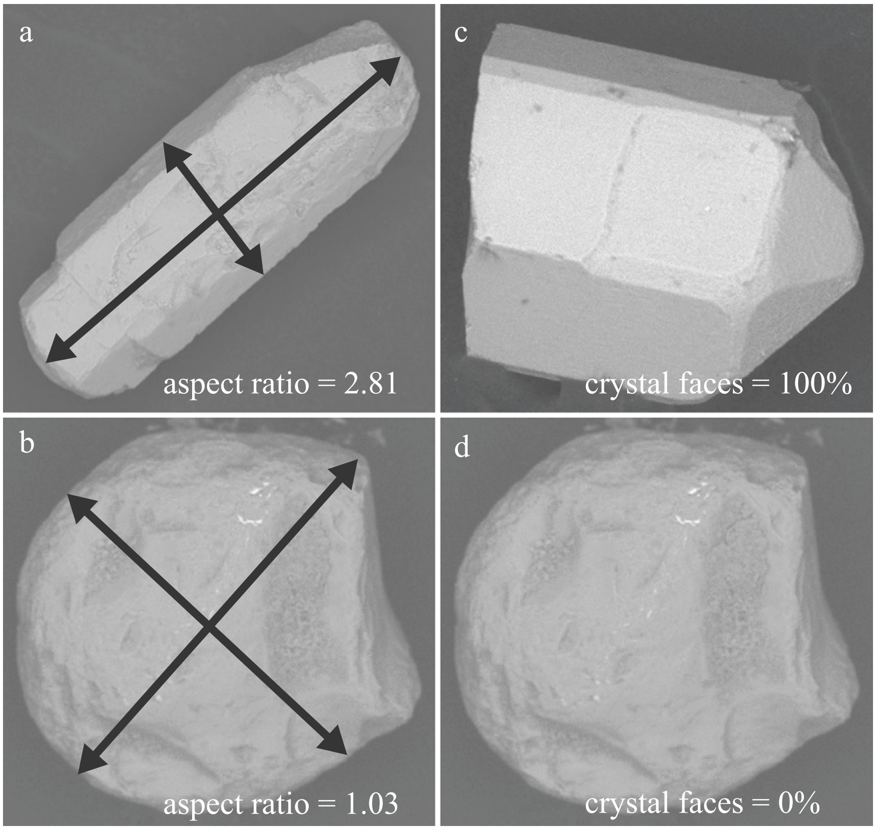

Fig. 2. We used two grain-shape metrics to quantify the weathering of isolated soil apatite grains: aspect ratio (a–b) and percent crystal faces (c–d). The aspect ratio differentiates between elongated grains (a) and rounded grains (b), and percent crystal faces differentiates between grains with intact faces (c) and grains without any visible faces (d).

The contrast in soil P between basins in Taylor Valley has been explained by spatial patterns of glacially deposited parent material, specifically the abundance of P-rich volcanic erratics found within the Fryxell Basin (Bate et al., 2007; Heindel et al., 2017). Kenyte, a rare porphyritic phonolite that is found scattered throughout the Fryxell Basin, contains abundant apatite within its matrix (Haskell et al., 1965; Gudding, 2003). However, it has also been suggested that rates of apatite weathering are higher in the Fryxell Basin due to higher levels of soil moisture and biological activity (Blecker et al., 2006; Bate et al., 2007; Heindel et al., 2017). It remains unclear whether the elevated levels of available soil P in the Fryxell Basin are due to a large amount of kenyte-derived apatite, faster rates of apatite weathering across all parent materials, or some combination of these two factors.

To differentiate among these scenarios, it is necessary to quantify the degree of weathering experienced by individual soil apatite grains. Scanning electron microscopy (SEM) allows us to see the surfaces of isolated minerals in exquisite detail, revealing complex morphologies that contain information about grain weathering histories. Etch pits, small depressions on mineral surfaces that form due to chemical dissolution, become larger and more abundant with increased weathering (e.g. Foellmi et al., 2009). Etch pit morphology is often dictated by mineral structure and can reveal processes involved in mineral dissolution (Dorozhkin, 1995; Kwon et al., 2008; Dorozhkin, 2012). For instance, in batch reactor experiments, apatite etch pits that formed in the presence of microbes developed rounder morphologies than etch pits that formed under abiotic conditions (Welch et al., 2002). In the MDVs, etch pits formed on the surfaces of pristine biotite grains after spending only one season within stream channel sediments, even though limited weathering is often anticipated in such cold conditions (Maurice et al., 2002). While the biotite results highlight the potential of etch-pit formation and mineral dissolution in the stream channels of the MDVs, they also point to the fact that most of the research on mineral weathering in this region has been focused on silicate minerals within saturated hyporheic sediments.

In this study, we consider the role of apatite biogeochemical weathering in shaping patterns of soil P availability in Taylor Valley. We use SEM to quantify the morphology and surface etching of individual apatite grains to determine whether the degree of apatite weathering differs between the Bonney and Fryxell Basins as well as saturated and dry soil sediments. If the rate of apatite weathering controls P availability in Taylor Valley, we would expect apatite grains from the Fryxell Basin to be more visibly weathered than grains from the Bonney Basin. Because the dissolution of apatite requires liquid water, we also predicted that apatite grains from saturated sediments would show more signs of biogeochemical weathering than grains from dry soils. This grain-scale approach provides a new perspective on P cycling in the MDVs and highlights potential controls on apatite weathering beyond our study region.

2. Methods

2.1. Regional setting

The McMurdo Dry Valleys are the largest region of ice-free land on the Antarctic continent (Levy, 2013). Mountain glaciers, perennially ice-covered lakes, ephemeral streams, and dry soils comprise the McMurdo Dry Valleys ecosystem. The soils, the focus of this study, are host to a diverse assemblage of tardigrades, rotifers, nematodes, and bacteria (Freckman and Virginia, 1997; Cary et al., 2010). In the McMurdo Dry Valleys, soil organisms survive some of the coldest and driest conditions on the planet; the mean annual air temperature is approximately $-19\,^{\circ}\mathrm{C}$ and the mean annual water-equivalent precipitation (all of which falls as snow) is 3 to 50 $\mathrm{mm\,yr^{-1}}$ (Doran et al., 2002; Fountain et al., 2009). In addition, liquid water and soil nutrients are extremely limiting, and soil pH and salinity are both high (Claridge and Campbell, 1977; Burkins et al., 2001).

Taylor Valley, the main field site of the McMurdo Dry Valleys Long-Term Ecological Research project, extends east from the Taylor Glacier,

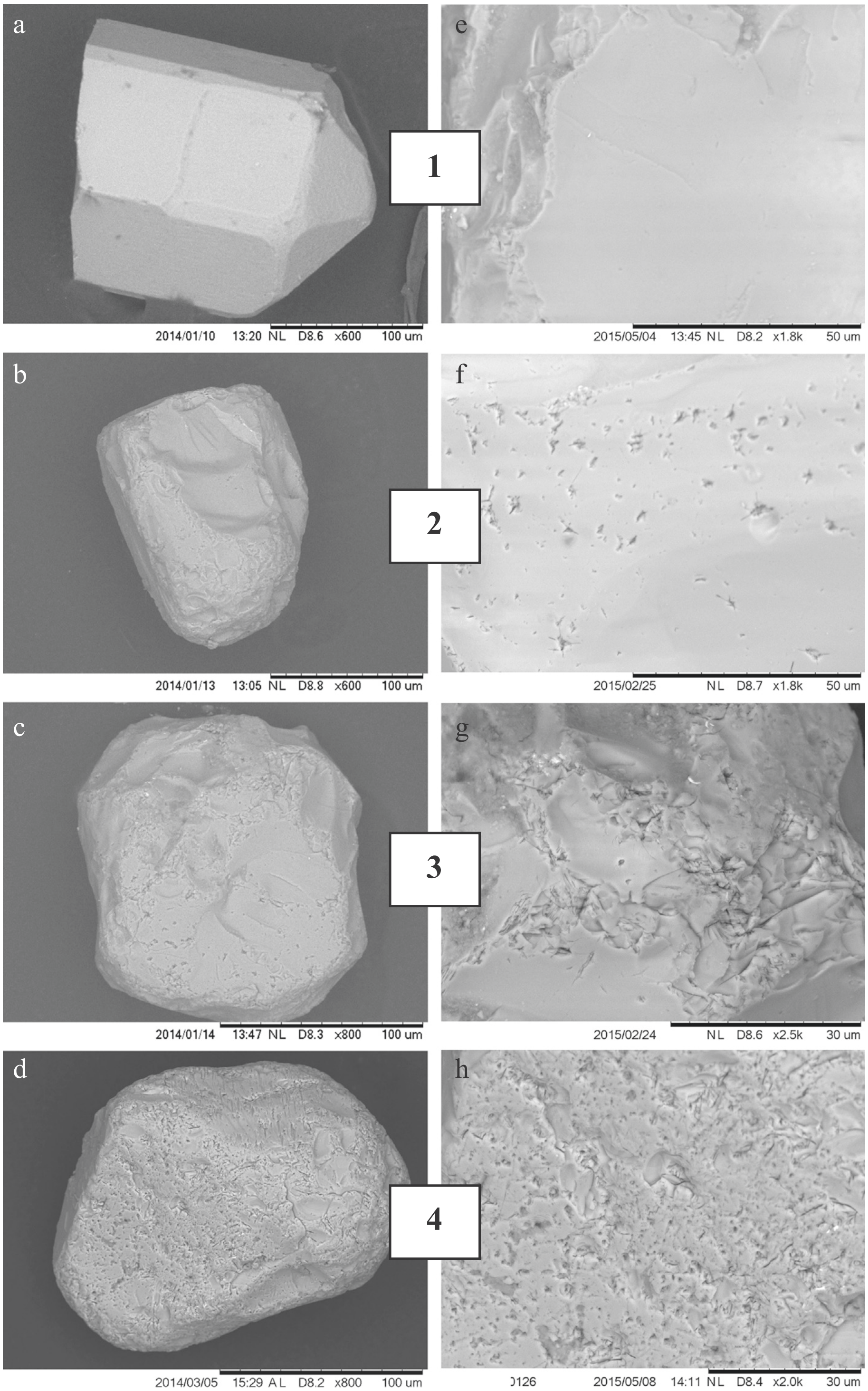

Fig. 3. Scanning electron microscope images that illustrate the pitting index we developed to quantify the prevalence of etch pits on apatite grain surfaces. We show images of the entire grains (a–d) as well as close-up images of the etch pits (e–h).

an outlet glacier of the East Antarctic Ice Sheet, to the McMurdo Sound (Fig. 1). In this study, we focus on two distinct drainage basins in Taylor Valley: the Fryxell Basin in the east, draining into Lake Fryxell, and the Bonney Basin in the west, draining into Lake Bonney (Fig. 1). Although they are located within the same valley, the two basins have contrasting glacial histories. Bonney drift, the parent material in the Bonney Basin, was deposited during an advance of the Tayler Glacier 70,000 to 130,000 years ago (Higgins et al., 2000a). On the other hand, Ross Sea drift, the parent material in the Fryxell Basin, was deposited by a grounded Ross Sea Ice Sheet and a proglacial lake system during the Last Glacial Maximum, 19,000 to 26,500 years ago (Hall et al., 2000). Ross Sea drift is distinct from Bonney drift not only in age but also because it contains volcanic erratics carried across the McMurdo Sound. These volcanic rocks, including the rare porphyritic phonolite called kenyte, are important to this study because they contain unusually high amounts of the mineral apatite (Haskell et al., 1965; Gudding, 2003).

2.2. *Soil sampling and chemistry*

During the 2012–2013 austral summer, we collected 9 surface soil samples for apatite separation (Fig. 1, Table 1). In the Fryxell Basin, we collected 2 samples at low elevation near the mouth of Von Guerard

Table 2
Soil chemistry results. Samples are grouped by basin and then ordered by elevation.

Sample ID	Basin	Moisture class	HCl-extractable P (g kg^{-1})	$NaHCO_3$-extractable P (mg kg^{-1})	pH	Electrical conductivity (μS/cm)
LBD1	Bonney	Dry	0.27	1.16	9.15	392
LBW1	Bonney	Saturated	0.36	0.74	9.05	50.8
LBW2	Bonney	Saturated	0.46	2.76	8.91	59.6
LBD2	Bonney	Dry	0.44	0.46	9.85	66.2
LFD1	Fryxell	Dry	1.20	9.65	10.3	865
LFW1	Fryxell	Saturated	1.43	2.77	9.12	36.1
LFD3	Fryxell	Dry	0.52	0.90	9.22	33.6
LFW3	Fryxell	Saturated	0.68	3.39	8.48	13.68
LFD2	Fryxell	Dry	0.69	2.58	8.96	40.1

Stream and 3 samples at high elevation along the southern valley wall. In the Bonney Basin, we collected 2 samples at low elevation near Wormherder Creek and 2 samples at high elevation along the southern valley wall. At each sampling location where possible, we collected one fully saturated sediment sample from the hyporheic zone and one dry soil sample adjacent to the stream channel. Saturated sediments were collected from well-developed stream channels and have likely experienced elevated moisture conditions over long timescales. Dry soil samples were collected from locations outside of the stream channels that have likely rarely experienced flowing water. At the high elevation sites, paired samples were not located as closely together as at the low elevation sites, but were still either saturated sediment or dry soil. For analyses, we classify samples by basin and by the moisture classes “saturated” and “dry.” After collection, samples were frozen and shipped to Dartmouth College, where we conducted laboratory analyses.

For all 9 surface soil samples, we measured labile and Ca-bound phosphorus, pH, and electrical conductivity (EC). The extraction and analytical methods we used are detailed in Heindel et al. (2017), a region-wide study looking at variability in soil phosphorus content and availability throughout the McMurdo Dry Valleys. In brief, we performed an 0.5 M $NaHCO_3$ extraction to quantify labile phosphorus and a 1.0 M HCl extraction followed by a persulfate digestion to target Ca-bound phosphorus. The phosphorus content of both labile and Ca-bound extracts was analyzed colorimetrically on a Lachat QuikChem 8500 flow injection auto analyzer (Lachat Instruments, Has Company, Loveland, CO). We also measured pH and EC of sieved ($<$ 2 mm) soil samples in 1:2 and 1:5 soil:deionized water slurries, respectively.

2.3. Apatite separation and scanning electron microscopy

To isolate individual apatite grains from soil samples, we used standard sieving, heavy-liquids, and magnetic mineral separation techniques. First, we sieved dry soil samples to isolate the 125–250 μm grain fraction. We focused on the coarse-silt to fine-sand fraction to improve our ability to isolate apatite grains, since apatite grains are typically not found at a size $>$ 250 μm in common MDVs lithologies, and because heavy-liquids and magnetic separation are difficult to perform on clay- and silt-sized particles that are $<$ 125 μm. Second, we used lithium heteropolytungstate heavy liquids (LST) at 2.85 g ml^{-1} to separate light minerals from the heavy minerals. Since apatite has a specific gravity of 3.16–3.22, apatite remained in the heavy fraction. Next, we used magnetic separation to remove magnetic minerals. We first used a hand magnet to remove strongly magnetic minerals, and then we repeatedly ran our samples through a S.G. Frantz® magnetic susceptibility laboratory separator increasing the strength up to 1.4 A. Apatite is non-magnetic up to 1.5 A, so it remained in the non-magnetic fraction. Finally, we handpicked apatite grains under a light microscope and secured them onto Scanning Electron Microscope (SEM) stubs using black carbon tape.

Using a Hitachi TM3000 SEM with Bruker energy dispersive X-ray spectroscopy (EDS), we confirmed the composition of individual apatite grains. We captured SEM images of each apatite grain for the weathering metrics described below. We also captured SEM images of etch pit morphologies, using both the Hitachi TM3000 SEM as well as a FEI Quanta FEG 250 Field Emission SEM at The Ohio State University.

2.4. Weathering metrics and etch-pit morphology

To quantify the degree of physical and chemical weathering of isolated soil apatite grains, we developed three metrics that characterize grain shape and micromorphology: aspect ratio, percent crystal faces, and chemical etching (Figs. 2 and 3). We defined the aspect ratio as the length of the long axis of the grain divided by the length of the short axis, giving a measure of how elongated grains are (Fig. 2). We defined the percent crystal faces metric as the percent of the total visible grain area that was a recognizable crystal face (Fig. 2). We analyzed SEM images with the software ImageJ to calculate the aspect ratio and percent crystal faces for each isolated apatite grain (Schneider et al., 2012). For the pitting index, we modified a qualitative weathering index for apatite used in Foellmi et al. (2009) to better capture the variability we saw in our grains (Fig. 3). Our pitting index ranged from 1 (grains with few to no etch pits) to 4 (grains with etch pits covering the entire grain surface). To determine the pitting level for each grain, we examined each grain thoroughly using SEM.

We used Analyses of Covariance (ANCOVAs) to test if basin, moisture class, and their interaction significantly explained variance in the aspect ratio and percent crystal faces of apatite grains. Because the pitting index is an ordered categorical variable, we used an ordinal logistic regression to test the effect of basin, moisture class, and their interaction on the pitting index. We tested for correlations between the mean weathering metrics at each site and the two soil P fractions (labile and Ca-bound), pH, EC, and sample elevation using Pearson's correlation coefficient.

2.5. Data availability

A dataset with the weathering metrics for each apatite grain is available for download from the Environmental Data Initiative: https://doi.org/10.6073/pasta/60981e56195e6742d727cf691912b663 (Heindel, 2017).

3. Results

3.1. Soil chemistry results

We determined the $NaHCO_3$-extractable (labile) and HCl-extractable (Ca-bound) P concentrations, pH, and EC results for the 9 surface soil samples analyzed in this study to make comparisons with the grain-scale weathering metrics. The soil chemistry results presented here have also been previously published in Heindel et al. (2017) as part of a larger region-wide dataset on phosphorus availability in the McMurdo Dry Valleys. Due to our limited sample size and the high spatial heterogeneity of MDVs soil geochemistry, we report only

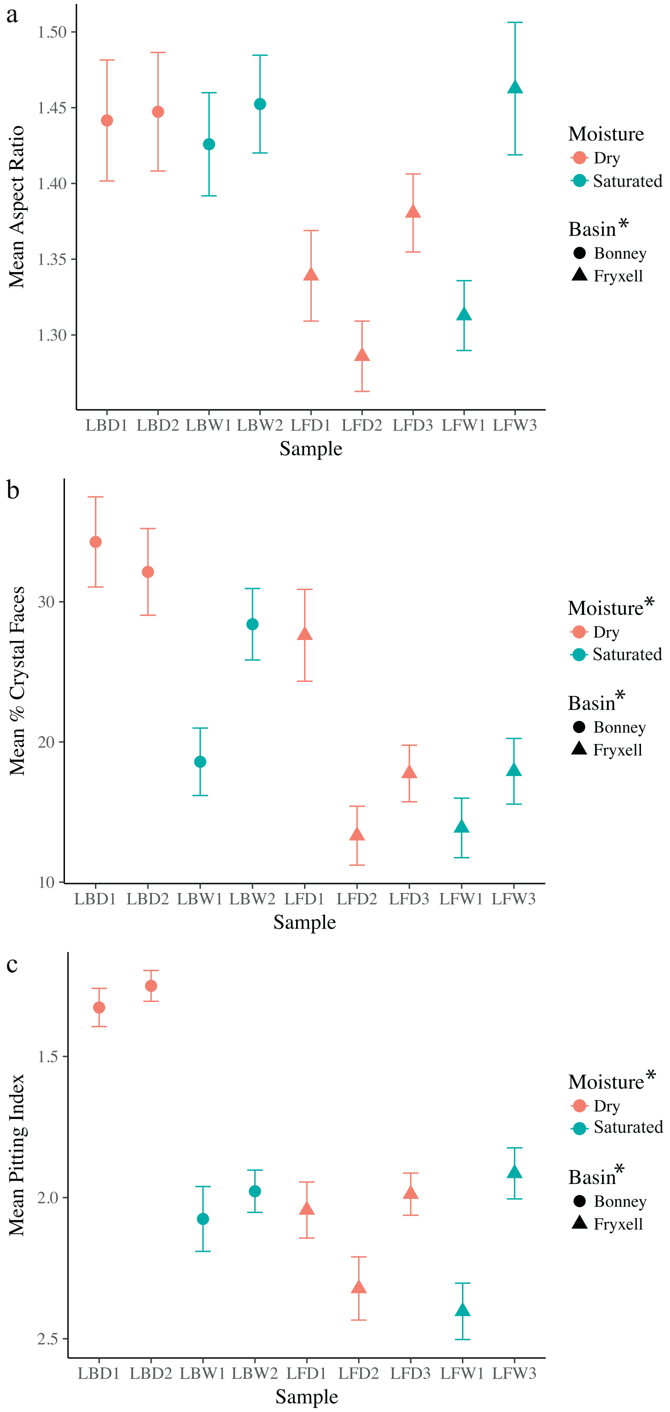

Fig. 4. Results of the three weathering metrics for all samples. Each point is the mean value for apatite grains isolated and analyzed from each of the 9 soil samples (n = 49–87 per sample). Error bars are plus and minus one standard error. We show results for aspect ratio (a), percent crystal faces (b), and pitting index (c). Stars denote which factors were significant explanatory variables, based on ANCOVAs. For percent crystal faces and pitting index, the interaction between moisture class and basin was also a significant explanatory variable.

general trends here. A more rigorous statistical analysis of soil P concentrations across Taylor Valley is presented in Heindel et al. (2017).

$NaHCO_3$-extractable and HCl-extractable P concentrations in soils were generally higher in the Fryxell Basin than in the Bonney Basin. In this small group of samples, $NaHCO_3$-extractable P concentrations were highly variable, ranging from 0.46 to 2.76 mg kg^{-1} dry soil in the Bonney Basin and from 0.9 to 9.65 mg kg^{-1} dry soil in the Fryxell Basin (Table 2). HCl-extractable P concentrations ranged from 0.27 to 0.44 g kg^{-1} dry soil in the Bonney Basin and from 0.52 to 1.43 g kg^{-1} dry soil in the Fryxell Basin (Table 2).

As is the case for soils across the McMurdo Dry Valleys, the pH values of our samples were basic, and soils displayed a wide range of EC. Soil pH ranged from 8.48 to 10.3 across both basins, with no noticeable difference between basins (Table 2). EC also did not vary between basins, and ranged from 13.68 to 865 μS (Table 2).

3.2. *Apatite chemistry*

Using SEM-EDS to confirm the composition of each apatite grain, we were successful in isolating and identifying 49–87 apatite grains for each soil sample (Table 1). All isolated apatite grains were analyzed for aspect ratio, percent crystal faces, and pitting index.

For all sites and moisture classes, isolated soil apatite grains had a consistent fluorapatite composition. Across all grains (n = 611), the normalized weight % for Ca was 30–33, 12–14 for P, 44–48 for oxygen, and 4–5 for fluorine. We measured only trace amounts ($<$ 0.2%) of chlorine. With the semi-quantitative resolution of EDS, we found no significant differences in the elemental composition of apatite grains among sites or moisture levels.

3.3. *Weathering metrics*

Isolated apatite grains from the Fryxell Basin were rounder, less intact, and more chemically etched than grains from the Bonney Basin (Fig. 4). The ANCOVAs for aspect ratio and percent crystal faces, as well as the ordinal logistic regression for pitting index, all showed that basin was a significant explanatory variable ($P < 0.001$), with Fryxell Basin grains showing more evidence of physical and chemical weathering.

Grains from saturated samples were less intact and more chemically etched than grains from dry samples, especially in the Bonney Basin. The ANCOVA for percent crystal faces and the ordinal logistic regression for pitting index both showed that moisture class as well as the interaction between basin and moisture class were significant explanatory variables ($P < 0.001$). Moisture class had a large effect on the degree of apatite weathering in the Bonney Basin, whereas in the Fryxell Basin saturated and dry samples were more similar (Fig. 4).

The only significant correlation between the weathering metrics and soil chemistry was a negative correlation between aspect ratio and HCl-extractable P ($R = -0.68$, $P = 0.045$). Samples with round grains (low aspect ratios) tended to have higher levels of HCl-extractable P. There were no significant correlations between the weathering metrics and $NaHCO_3$-extractable P, pH, EC, or sample elevation.

3.4. *Etch pit morphology*

We observed many different morphologies of etch pits (Fig. 5). Some etch pits were clearly hexagonal (Fig. 5a), reflecting the unweathered hexagonal mineral structure of apatite. Other etch pits and dissolution features were not hexagonal and lacked any clear crystallographic structure. Common non-hexagonal etch-pit morphologies included crescent-shaped grooves reminiscent of glacial chatter marks (Fig. 5b), deep grooves emanating from a single origin (Fig. 5c), deep cracks (Fig. 5d), coalesced etch pits (Fig. 5e), shallow nicks (Fig. 5f), shallow parallel grooves (Fig. 5g), and stepping features (Fig. 5h).

While we observed all etch-pit morphologies in saturated and dry samples from both basins, we noticed a few trends. To quantify these trends, we thoroughly examined the visible portion of each grain and tallied all instances of etch pits with the morphologies described above. Single grains could have multiple types of etch pit morphologies; each morphology was tallied as a separate instance, resulting in 672 discrete morphology observations among the 611 analyzed grains. We express the prevalence of each morphology as a percentage of the total number

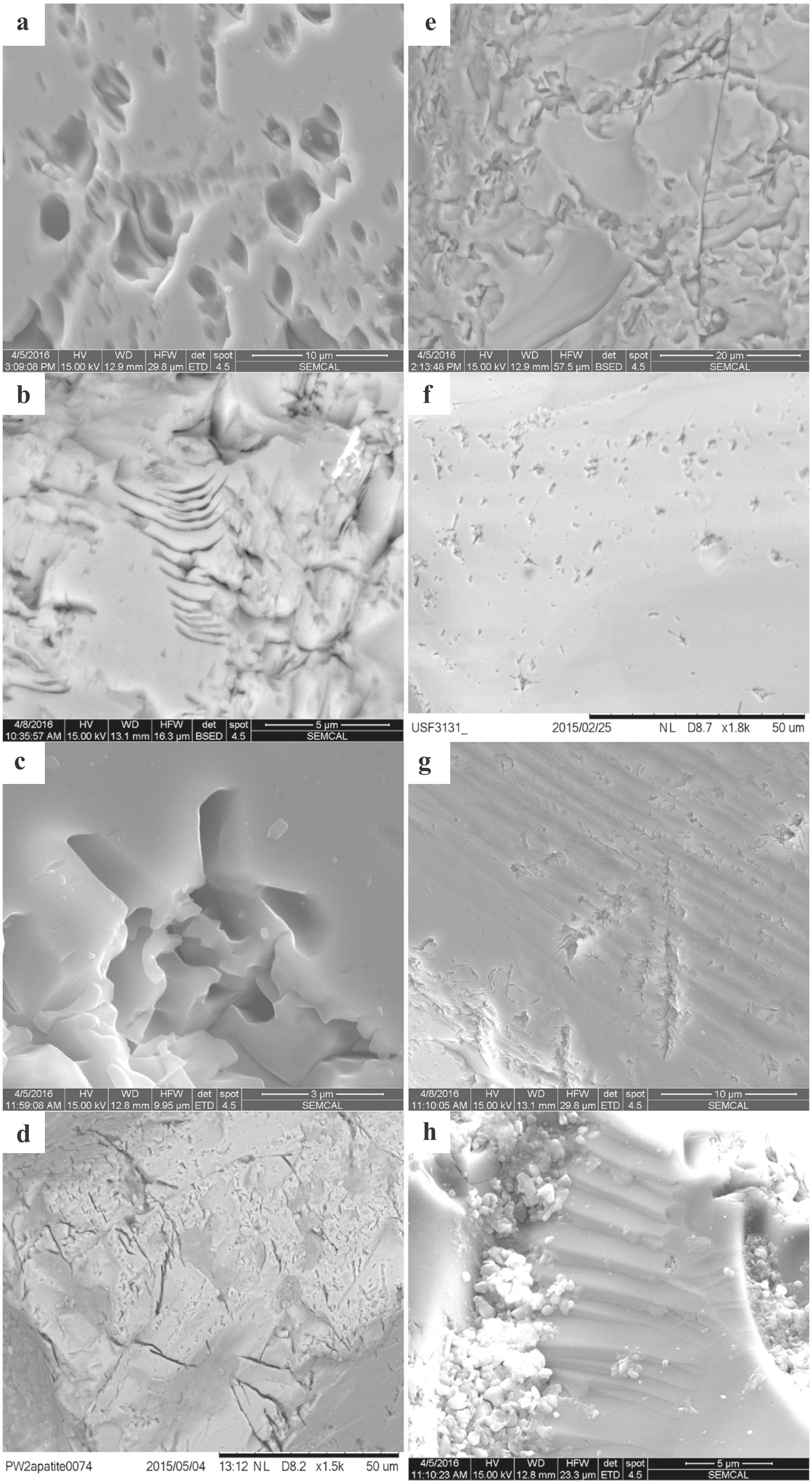

Fig. 5. SEM images showing the range of etch pit morphologies that we observed on apatite grain surfaces: hexagonal (a), chatter marks (b), deep grooves emanating from a single origin (c), deep cracks (d), coalesced etch pits (e), shallow nicks (f), shallow parallel grooves (g), and stepping features (h). Note the different scale bars at the bottom of each image.

of observations for a given moisture class or site, to normalize for differences in degree of etching (Table 3). Dry samples and samples from the Bonney Basin were similar in that hexagonal etch pits and stepping features were the most common morphologies (Table 3). In contrast, saturated samples and Fryxell samples were similar in that coalesced etch pits were the most common etch pits (Table 3).

Table 3
Percentages of etch pit morphologies for each sample type: dry and saturated soil locations and the Bonney and Fryxell Basins. Percentages were calculated based on the total instances of identifiable etch-pit morphologies for each moisture class or basin. 672 morphology observations were made across 611 grains. Letters after each morphology match those in Fig. 5.

Etch pit morphology	Dry	Saturated	Bonney	Fryxell
Hexagonal (a)	20	9	21	10
Chatter Marks (b)	6	3	3	6
Grooves single origin (c)	6	4	4	6
Deep cracks (d)	21	9	15	15
Coalesced (e)	14	34	6	36
Shallow nicks (f)	12	22	21	12
Parallel grooves (g)	4	8	7	5
Stepping features (h)	18	11	23	9
	(100%)	(100%)	(100%)	(100%)

4. Discussion

4.1. Apatite weathering metrics and etch-pit morphologies

Although it is impossible to know the morphology of apatite grains when they are first released from parent rocks, certain sediment grain morphologies have been associated with increased weathering (e.g. Berner and Holdren, 1979; Mahaney et al., 1996; Foellmi et al., 2009). Rounded grains and grains with no intact crystal faces have likely experienced more physical and chemical weathering than euhedral grains. Similarly, grains covered with deep etch pits have likely experienced more chemical weathering than grains with smooth unaltered surfaces (Foellmi et al., 2009). Apatite grains separated from the soils of Taylor Valley showed clear signs of physical and chemical weathering, even though apatite is relatively insoluble at the basic pH of the bulk soil samples. The round morphologies, lack of crystal faces, and high degree of etch pits observed on apatite grains from the Fryxell Basin support the hypothesis that faster rates of apatite weathering may contribute to the elevated levels of available P found there.

There are several reasons why apatite grains in the Fryxell Basin may have experienced higher rates of physical and chemical weathering than grains in the Bonney Basin. The difference in physical weathering may reflect legacy glacial conditions rather than current processes. In the Bonney Basin, apatite grains were deposited by the cold-based Taylor Glacier (Higgins et al., 2000b). With only restricted physical weathering due to the glacier being frozen to its bed, apatite grains may have retained their elongated morphology with intact crystal faces. In contrast, apatite grains in the Fryxell Basin were deposited by the warm-based Ross Sea Ice Sheet (Hall et al., 2000). In this case, extensive abrasion along a dynamic glacier bed may have rounded the apatite grains and removed crystal faces. The glacial histories of the two basins may also lead to differences in chemical weathering, since Fryxell grains may have been preconditioned for easy chemical dissolution along weaknesses created through physical abrasion (Foellmi et al., 2009). For instance, the etched chatter marks (Fig. 5b), which are slightly more common on Fryxell grains (Table 3), are an example of physical abrasion leading to chemical dissolution. These features, which have previously been identified as a sign of initial dissolution on feldspar grains, begin as shallow physical cracks formed from grain-to-grain contact and are subsequently chemically enlarged and deepened (Berner and Holdren, 1979).

Further, soil moisture, a requirement for apatite dissolution, seems to play a more limiting role in the Bonney Basin than the Fryxell Basin. While Fryxell apatite grains showed high levels of etching across moisture classes, Bonney grains from dry soil samples were minimally etched. This difference between basins may reflect the glacial histories discussed above, as well as current climate conditions. Soils in the Bonney Basin, located farther inland, receive less precipitation than the Fryxell Basin and tend to be more water-limited (Barrett et al., 2004; Fountain et al., 2009). In dry Bonney soils, there may not be sufficient moisture to chemically weather the intact apatite grains. In contrast, in the Fryxell Basin, the combination of increased precipitation and physically preconditioned apatite grains may allow for apatite dissolution even where soil moisture is minimal. In addition, the broader morphology of the Fryxell Basin results in longer streams with lower slopes than in the Bonney Basin. This difference in basin shape gives apatite grains in the Fryxell Basin more exposure to liquid water and provides more time for weathering to occur.

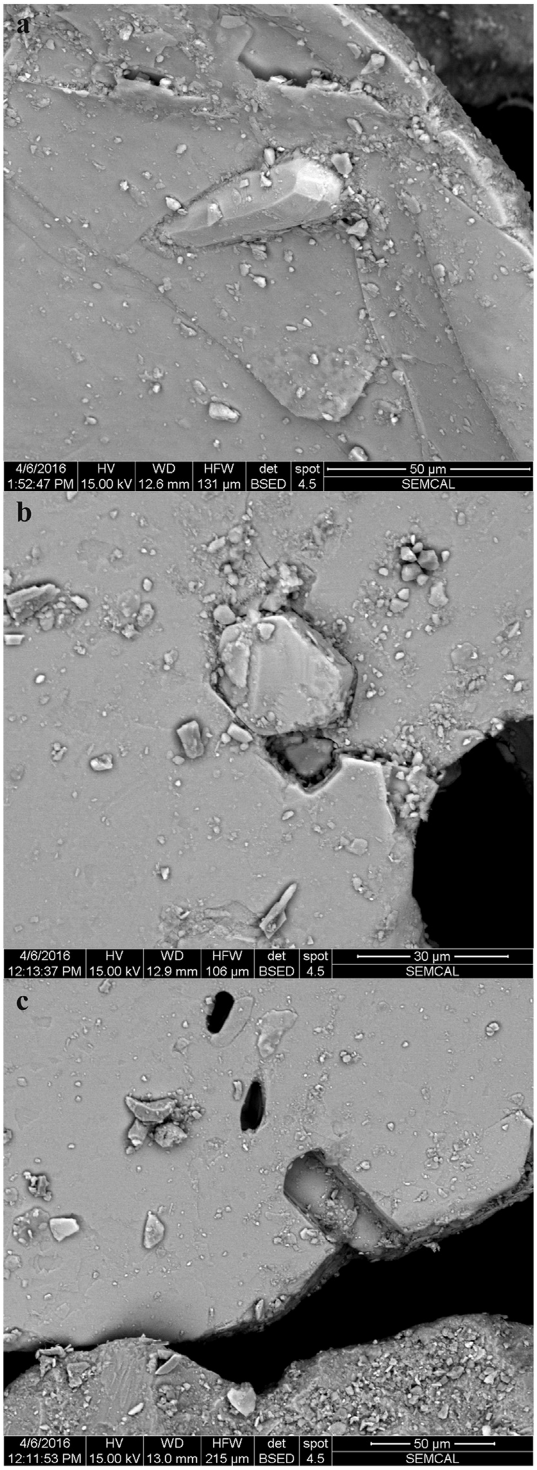

Fig. 6. SEM images of biotite grains with small (scale bar at bottom right) apatite inclusions (a, b) and with cavities likely once filled with apatite inclusions (c).

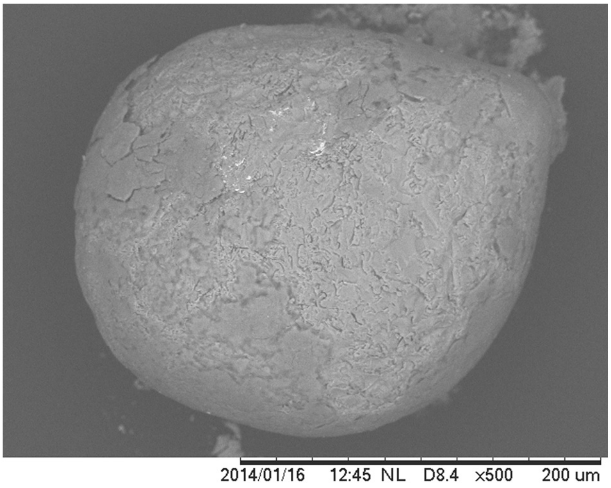

Fig. 7. Heavily etched apatite grain partially covered in a clay film. Film is most noticeable in the top left of the image.

The lack of etch pits on apatite grains from dry Bonney soils may also reflect a difference in the chemistry of the soil solution. In laboratory studies of hydroxyapatite and fluorapatite dissolution in acid, etch pits stopped forming when Ca^{2+} was added to the solution, decreasing the rate of apatite dissolution (Dorozhkin, 1995, 2012). In Taylor Valley, Ca^{2+} concentrations measured in DI extracts from soil samples unrelated to this study were nearly an order of magnitude higher in the Bonney Basin ($38 \pm 13\,\mu g\,g^{-1}$ dry soil; mean ± standard deviation) than in the Fryxell Basin ($5 \pm 3\,\mu g\,g^{-1}$ dry soil; McMurdo Dry Valleys Long-Term Ecological Research, unpublished data). Similarly, while in general streams in Taylor Valley are enriched in Ca^{2+} relative to the world average, streams in the Fryxell Basin are not as enriched in Ca^{2+} as streams in the Bonney Basin (Welch et al., 2010). High concentrations of Ca^{2+} in Bonney Basin streams and soils may thus play a role in minimizing soil apatite weathering. In addition, any phosphate released by biogeochemical weathering into Bonney soils may quickly re-precipitate as apatite. Differentiating between primary rock-derived apatite and secondary apatite precipitated in the soil solution is an important area for future research.

We observed a wide range of etch pit morphologies that are unlike most apatite etch pits described in the literature. When hydroxyapatite and fluorapatite are dissolved in acid in abiotic conditions, etch pits are regular and hexagonal, dictated by the apatite crystal structure (Dorozhkin, 1995; Kwon et al., 2008; Dorozhkin, 2012). In our study, hexagonal etch pits are most common in dry samples and samples from the Bonney Basin, suggesting that the mode of apatite dissolution under these conditions is most similar to acidic abiotic laboratory experiments. However, hexagonal etch pits were relatively rare in our samples; most often the etch pits we observed were not clearly dictated by the apatite crystal structure. In some cases, as for the etched chatter marks described above, the morphology of etch pits may be controlled by previous physical weathering that the grains experienced. Etch pit morphology can also be altered by organic acids and the presence of microorganisms; sometimes etch pits directly take the shape of cells (Welch et al., 2002; Brehm et al., 2005; Foellmi et al., 2009; Ouyang et al., 2017). In a granodiorite weathering sequence in Australia, microorganisms were observed colonizing apatite grains (Taunton et al., 2000). Although we observed no cell-shaped etch pits or microorganisms, it is possible that the intricate etch pit morphologies may have formed due to biological interactions. Understanding the information contained in apatite etch pit morphologies could be a fruitful avenue for future research and may require laboratory experiments simulating the dry basic conditions of MDVs soils.

4.2. *Apatite weathering and soil chemistry*

The only correlation we observed between the apatite weathering metrics and the two soil P fractions was a negative correlation between HCl-extractable P and aspect ratio. While it may seem counterintuitive that soils with highly weathered apatite grains would contain more Ca-bound P, this correlation is driven by the difference between the two basins. Bonney samples cluster at one end of the correlation, with samples containing low HCl-extractable P concentrations and high aspect ratios. Within each basin, no correlation between HCl-extractable P and aspect ratio exists.

The lack of meaningful correlation between the apatite weathering metrics and the two soil P fractions (HCl- and $NaHCO_3$-extractable P) may be due to our limited sample size, but it may also be because the apatite grains we analyzed were in the restricted size fraction of 125–250 μm. While focusing on this size fraction allowed us to efficiently separate apatite grains from the bulk soil, there are likely many apatite grains in smaller size fractions. For instance, when we looked at soil grains from one of our samples under SEM prior to any mineral separation procedures, we observed numerous apatite inclusions within biotite crystals (Fig. 6). It is possible that dissolution of these apatite inclusions may contribute more to soil available P than the dissolution of the rarer large apatite grains we analyzed. Quantifying how apatite is distributed among soil grain sizes may be an important step in establishing the link between apatite weathering and total and available soil P concentrations.

We also observed no correlation between the apatite weathering metrics and soil pH and electrical conductivity. While we would expect to see increased apatite dissolution at a lower soil pH, bulk soil measurements may not accurately capture the micro-level pH at apatite mineral surfaces. For instance, in a study of quartz weathering, the formation of biofilms on grain surfaces locally altered the pH to favor quartz dissolution without changing the pH of the bulk soil (Brehm et al., 2005). If biofilms form on the surface of apatite grains, they could allow for apatite dissolution in a basic soil environment, decoupling the bulk soil chemistry from apatite weathering. Although our mineral separation procedures may have removed any biofilms from the apatite grain surfaces, we did observe a few apatite grains incased in a film of clay particles (Fig. 7). This observation suggests that the local conditions at the surface of apatite minerals may be distinct from the bulk soil chemistry, and may help explain how apatite dissolution can occur under basic conditions.

5. Conclusions

Apatite grains separated from saturated hyporheic sediments and dry soils in Taylor Valley, Antarctica, showed clear signs of physical and chemical weathering. Apatite grains from the Fryxell Basin, where total and available soil P concentrations are high, were more rounded, had fewer intact crystal faces, and were more chemically etched than apatite grains from the Bonney Basin. In the Bonney Basin, soil moisture appeared to limit apatite weathering, with little to no apatite dissolution occurring in the dry soils collected from that basin. The differences observed between the basins may be due to a combination of glacial history and current climate conditions. Apatite grains in the Fryxell Basin likely experienced more physical abrasion during transport by the warm-based Ross Sea Ice Sheet than the Bonney grains experienced during transport by the cold-based Taylor Glacier. Currently, grains in the Fryxell Basin may experience faster rates of chemical weathering due to this physical preconditioning and due to the wetter climate experienced by the eastern half of Taylor Valley. By focusing on the grain-scale characteristics of mineral apatite, we provide a new perspective on P cycling in the MDVs, one that highlights the role of apatite weathering in contributing available P to the soil ecosystem.

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