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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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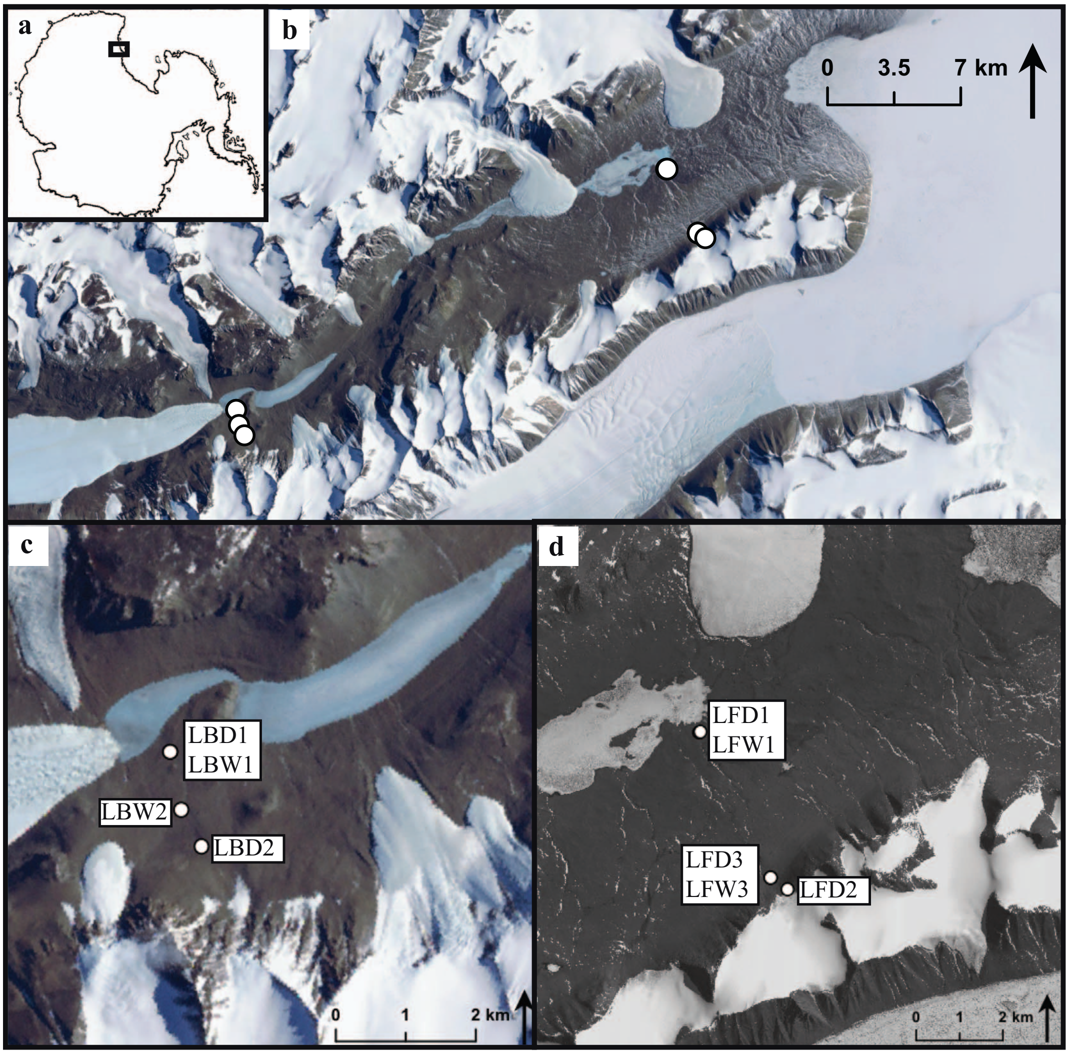

Fig. 1. Maps showing the location of the McMurdo Dry Valleys on the Antarctic continent (a), the sample locations in Taylor Valley (b), and close-ups of sample locations in the Bonney Basin (c) and the Fryxell Basin (d).

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).