



GEOSCIENCES

Soil pockets phosphatization and chemical weathering of sites affected by flying birds of Maritime Antarctica

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Abstract: The majority of ornithogenic soils studied in Antarctica focus on the influence of penguins, wherever little reports evaluated the influence of flying birds on soil genesis. This study aimed to characterize the morphologic, chemic, physic, mineralogic, and micromorphologic ornithogenic soil pockets influenced by flying birds in Snow Island, Maritime Antarctica. Fifteen soil pockets were selected, described, sampled and analyzed, these sites constitute the main areas with intense long-term terrestrial biological activity in Snow Island. In order to investigate the impact of phosphatization, we compared the soil pockets with the surrounding soils and soils affected by penguins. Zone of phosphatization have a high concentration of P, K, and Ca. The XRD patterns for the clay fraction of ornithogenic soils show that phosphate minerals are the main crystalline phases (leucophosphite, minyulite, fluorapatite, and apatite). We show that even under typical periglacial conditions, sites influenced by flying birds present active chemical weathering processes. The phosphatization release exchangeable bases and accelerate mineralogical and micromorphological transformations in soils. Under the current global warming trend and expected sea-level rise, the ornithogenic environments are susceptible to accelerated erosion rates and a great part of these hotspots may be lost for the open sea.

Key words: Global warming, nutrients hotspots, Ornithogenic soil, secondary minerals.

INTRODUCTION

Ornithogenic soils are composed by mineral and organic materials influenced by birds (Ugolini 1972, Simas et al. 2007). They often have a high content of gravels that has been transported by birds and are identified by other features such as bones, carcasses, eggshells, and feathers (IUSS Working Group WRB 2014). Ornithogenic soils from Maritime Antarctic are different from those of the Continent (Tatur & Myrcha 1984, Souza et al. 2014). In wetter climates, the substances leached/washed from the decomposition of guano react with the underlying substrate to form a broad phosphatized zone (Tatur

& Myrcha 1984, Simas et al. 2007, Lopes et al. 2021a). The ornithogenic soils of this region are unique in Antarctica and represent important sites where phosphatization is the main soil-forming process (Simas et al. 2007, Daher et al. 2019, Lopes et al. 2019). These conditions favor the formation of deep and clayey soils. However the genesis, processes, and transformation systems in phosphatized environments of flying birds are poorly known, compared with those under penguins.

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Birds activity during the short austral summer in Maritime Antarctica promotes sea-land interactions, transference of nutrients and organic matter (Simas et al. 2007). Large amounts of guano deposited by marine birds accumulate in ice-free areas (Simas et al. 2007, Daher et al. 2019), and these ornithogenic sites constitute the most important carbon reservoirs in Antarctic terrestrial ecosystems (Ugolini 1972, Simas et al. 2007), where vegetation growth is favorable (Tatur & Myrcha 1989, Cocks et al. 1999, Michel et al. 2006). These unique soils have granular and sub-rounded structures, mobilization of phosphates (illuviation) and secondary mineral formation, characterizing the phosphatization process (Simas et al. 2007).

Recent studies in periglacial environments aimed to understand how chemical weathering processes are associated with ornithogenic areas in Antarctica (Ugolini 1972, Tatur & Myrcha 1984, 1989, Tatur 1989, Tatur et al. 1997, Cocks

et al. 1999, Michel et al. 2006, Simas et al. 2007, Pereira et al. 2013, Schaefer et al. 2017, Daher et al. 2019, Lopes et al. 2021a, Rodrigues et al. 2021). The majority of ornithogenic soils studies focus on the influence of penguins (Ugolini 1972, Tatur & Myrcha 1984, 1989, Tatur et al. 1997, Simas et al. 2007, Schaefer et al. 2017), wherever little reports evaluated the influence of flying birds on soil genesis (Cocks et al. 1999).

This study purposed to analyze the phosphatization as a soil-forming process and unusual chemical weathering processes of sites affected by flying birds in the President Head Peninsula, Snow Island, Maritime Antarctica. These results enhance the debate on phosphatization and chemical weathering in periglacial environments and provide a baseline for the degree of ornithogenic influence with new approaches. Morphological, physical, chemical, mineralogical, and micromorphological characteristics of soils affected by flying birds were studied, allowing to improve the definitions, qualifiers, and diagnostic criteria of ornithogenic soils by the international WRB and Soil Taxonomy classification systems.

MATERIALS AND METHODS

Study area

President Head Peninsula (PHP) is located in the eastern sector of Snow Island (62° 43'54.7 "S - 61° 14'03.7"W), South Shetlands Archipelago, Maritime Antarctica (Figure 1). The Peninsula extends for 2.6 km in the east-northeast direction. The lithology varies from igneous to sedimentary rocks (basalts, andesites, tuffs, siltstones, mudstones, and sandstones) (Smellie et al. 1984, Torres et al. 1997).

The geomorphology of PHP reveals differences between paraglacial and periglacial landforms, and the area is dominated by a broad central plateau surrounded by talus slope and

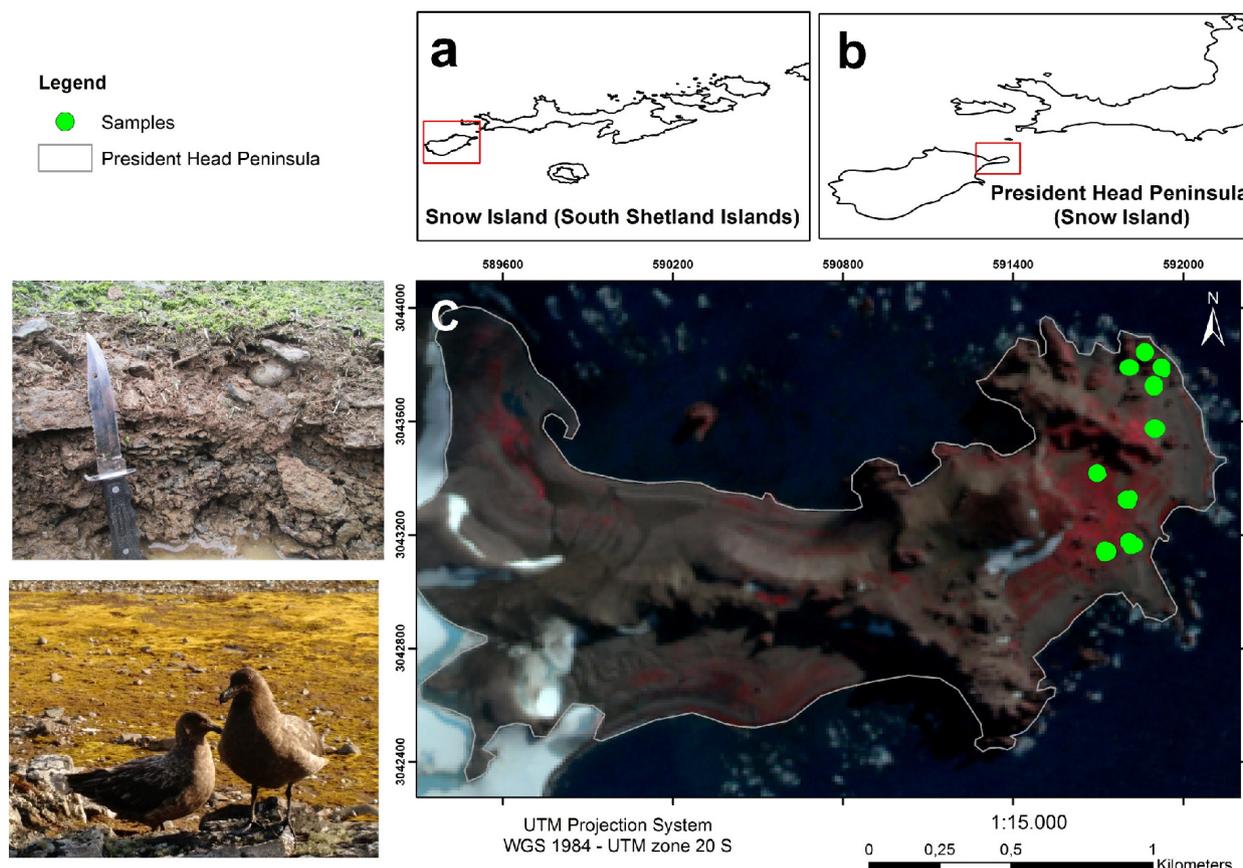


Figure 1. Localization of President Head Peninsula (c), Snow Island (b), South Shetlands Islands (a).

extensive coastal plains, where different levels of marine terraces occur. Lopes et al. (2021 in preparation) stratified President Head Peninsula into two landscape domains: 1) The sedimentary Paraglacial sector, at the western part of the Island, forming a dissected plateau, underlain by a sequence of Cretaceous sediments. These, active meltwater channels strongly erode this domain. 2) The igneous Periglacial sector, at the eastern part of the Island, with a flat-top plateau at about up to 70 m a.s.l., and permafrost and patterned ground above 50 m a.s.l.

During the summer 2017 expedition to Snow Island, we observed the local fauna, including numerous seal colonies, especially elephant seals and occasional penguins at the Holocene Beach. Other birds, like skuas and giant petrels have abundant nesting sites on the coastal

rocky outcrops, where soil pockets occur in microdepressions.

Sampling sites

Fifteen (15) surface soil pockets samples on coastal rock outcrops were selected during the 2017 austral summer in PHP. These sites constitute the main areas with intense long-term terrestrial faunal activity in Snow Island. Compound surface samples (0–20 cm) of present-day petrels and skuas nests were collected. The sampling design aimed to represent the influence of flying birds in the chemical weathering in the coastal domain.

Morphological, physical and chemical analyses

Samples were air-dried and sieved through a 2 mm sieve (Embrapa 1997). Sand, silt, and

clay content were determined by the pipette method after dispersion with 0.1M NaOH. Soil pH was determined in distilled water with a glass electrode in a 1:2.5 suspension (v/v soil and water) (Embrapa 1997).

The potential acidity (H+Al) was extracted by 1M ammonium acetate solution at pH 7.0. The content of exchangeable Ca^{2+} , Mg^{2+} , and Al^{3+} were determined in a 1M KCl extract. Exchangeable K^{+} and Na^{+} were determined after Mehlich-1 extraction. Phosphorus content (PM) was determined by a Mehlich-1 extraction solution. All chemical analyses complied with Embrapa (1997). The total organic carbon (OC) was determined by wet combustion (Yeomans & Bremner 1988).

Mineralogical and micromorphological analyses

The mineralogy of the clay fraction was determined by X-ray diffraction (XRD) on powdered samples. The XRD employed a PANalytical X'Pert Pro Diffractometer using $\text{Co K}\alpha$ radiation (40 kV, 30 mA) in a range of 5–70° 2 θ at an increment of 0.008° 2 θ steps per second. The clay fraction was submitted to the following treatments before X-ray analyzes: solubilize oxides and hydroxides with dithionite-citrate-bicarbonate (DCB), Mg saturation (MgCl_2), glycerol saturation, K saturation (KCl) at room temperature, heating of K-saturated samples to 350 °C, and then to 550 °C.

Undisturbed soil blocks were sampled (0–10 cm), dried at 50 °C and impregnated with cryetic resin. Impregnated samples were cut (0.5 cm thickness) using a diamond saw, polished and mounted onto glass slides. Thin sections of soils were described in a Zeiss microscope fitted with a digital camera. The micromorphological description was based on Stoops (2003) and Stoops et al. (2010).

Statistical analyses

Descriptive statistical analyses (mean, median, maximum, minimum, percentile 10 and 90, coefficient of variation, skewness and kurtosis) were performed. We used 17 samples of ornithogenic soils derived from penguin activities studied by Simas et al. (2007), Pereira et al. (2013), Simas et al. (2015), Daher et al. (2019) and 15 samples (Table I) of ornithogenic soils affected by airborne birdlife nesting of Snow Island, all located in Maritime Antarctica. The whole procedure to examine the descriptive statistical analysis was performed using the software STATISTICA (version 8.0).

In order to investigate the impact of phosphatization in the study area, we compared the soil pockets with the surrounding soils, presenting results of two non-ornithogenic reference pedons, respectively on marine terrace and upper plateau.

RESULTS

Morphological, physical and chemical properties

The ornithogenic soil pockets of PHP showed a mean of 46% of gravels (Table I), with textural range from clay loam to loamy sand, while sandy clay loam is the main soil texture (Table I). In general, soils have dark to olive gray colors (Table I). The soils have high mean contents of sand (54.6%), followed by 20% clay and 16.8% silt. Clay values are 1.65 higher than non-ornithogenic soils (Table I).

Ornithogenic soil pockets have an acidic reaction, with pH (water) ranging from 4.2 to 5.9, OC values reaching 40.6 dag kg^{-1} , usually eutrophic (mean 54.6%), with high levels of Mehlich-1 extractable-P (4503.7 mg dm^{-3}) and high Na^{+} (mean 739.2 mg dm^{-3}) (Table II). The mean contents of exchangeable Ca (7.5 $\text{cmol}_c \text{ dm}^{-3}$), K

Table 1. Morphological and physical properties of the ornithogenic soil pockets and reference samples from President Head Peninsula.

Sample	Gravel	Coarse Sand	Fine Sand	Silt	Clay	Texture	Color (dry)				Color (wet)	
							5Y	3/1	5Y	Very Dark Gray	5Y	4/2
SP 1	44,8	56,7	9,2	15,6	18,5	sandy loam	5Y	3/1	Very Dark Gray	5Y	4/2	Olive Gray
SP 2	53,4	71,8	11,5	7,7	9,1	loamy sand	5Y	5/2	Olive Gray	10YR	2/1	Black
SP 3	29,6	36,1	12,3	26,9	24,7	sandy clay loam	2,5Y	3/2	Very Dark Grayish Brown	10YR	3/3	Dark Brown
SP 4	27,3	66,7	6,7	9,0	17,6	sandy loam	2,5Y	3/1	Very Dark Gray	2,5Y	3/1	Very Dark Gray
SP 5	28,0	66,3	6,7	11,2	15,8	sandy loam	5Y	3/1	Very Dark Gray	2,5Y	3/1	Very Dark Gray
SP 6	77,0	45,3	8,2	22,9	23,6	sandy clay loam	5Y	6/2	Light Olive Gray	2,5Y	4/2	Dark Grayish Brown
SP 7	58,6	53,6	9,4	17,7	19,3	sandy loam	5Y	2,5/1	Black	5Y	3/1	Very Dark Gray
SP 8	66,4	47,4	7,1	22,9	22,6	sandy clay loam	5Y	3/1	Very Dark Gray	5Y	2,5/1	Black
SP 9	53,3	23,4	10,5	39,1	27,1	clay loam	5Y	4/1	Dark Gray	5Y	4/1	Dark Gray
SP 10	45,6	55,4	8,5	20,1	16,1	sandy loam	5Y	3/2	Dark Olive Gray	5Y	3/2	Dark Olive Gray
SP 11	41,6	47,2	10,8	22,9	19,1	sandy loam	5Y	4/2	Olive Gray	2,5Y	3/1	Very Dark Gray
SP 12	55,5	54,6	8,5	11,3	25,6	sandy clay loam	5Y	4/1	Dark Gray	2,5Y	3/3	Dark Olive Brown
SP 13	9,1	79,5	5,6	3,8	11,1	loamy sand	5Y	5/2	Olive Gray	2,5Y	3/2	Very Dark Grayish Brown
SP 14	50,7	46,4	8,4	15,5	29,6	sandy clay loam	5Y	4/2	Olive Gray	2,5Y	4/3	Olive Brown
SP 15	49,9	68,2	5,2	6,1	20,6	sandy clay loam	5Y	4/1	Dark Gray	2,5Y	3/3	Dark Olive Brown
Mean (n=15)	46,0	54,6	8,6	16,8	20,0	-	-	-	-	-	-	-
SD	17,1	14,6	2,1	9,3	5,7	-	-	-	-	-	-	-
Median	49,9	54,6	8,5	15,6	19,3	-	-	-	-	-	-	-
Non ornithogenic soil on marine terrace	40,3	60,0	18,6	9,2	12,1	sandy loam	2,5Y	4/3	Olive Brown	10YR	2/2	Very Dark Brown
Non ornithogenic soil on plateau	24,5	56,5	23,2	8,1	12,1	sandy loam	2,5Y	5/2	Grayish Brown	10YR	3/2	Very Dark Grayish Brown

(278.9 mg dm⁻³) and H+Al (11.8 cmol_c dm⁻³) were higher in soil pockets than non-ornithogenic soils on the marine terrace (2.0, 2.2 and 1.2 times higher, respectively) (Table II).

Comparison between sites affected by flying birds versus penguins

In Maritime Antarctica, nutrient availability is greatly enhanced by the vast guano deposition promoted by marine birds, and the phosphatization (Michel et al. 2006, Simas et al. 2007, Pereira et al. 2013, Daher et al. 2019, Rodrigues et al. 2019). Descriptive statistics demonstrate that soil pockets affected by flying birds activity show higher mean and median values of clay, P, K, Ca, Mg, BS, CEC and OC, compared to classical ornithogenic soils affected by penguin activity (Table III).

The comparative data demonstrated higher values of Al, H+Al, and Al saturation in penguin nesting areas. High values of H+Al can indicate a high organic matters and leaching degree, as reported by Daher et al. (2019). The deeper ornithogenic soils associated with penguins have high losses through leaching, with intense downward water percolation through the soil.

Soil pockets affected by flying birds show the highest extreme values (percentile 10), ornithogenic soils in penguin areas show the highest percentile 90 and coefficient of variation (CV). The shape of a probability distribution was platykurtic for all flying birds variables (except for Al saturation and CEC), and penguins areas (except for K and OC) (Table III). Skewness (a measure of the asymmetry of the probability distribution) was positive (the distribution is right-skewed) for penguin areas (except for sand) (Table III).

Mineralogical and micromorphological properties

X-ray diffraction patterns of the sand fraction show the presence of mordenite (0.34, 0.40, 0.65 nm), olivine (0.15, 0.18, 0.25, 0.28, 0.40 nm), biotite (0.21, 0.24, 0.32 nm), plagioclase (0.25, 0.28, 0.32, 0.40 nm), augite (0.14, 0.17, 0.21, 0.25, 0.28, 0.32 nm), ilmenite (0.14, 0.17, 0.19, 0.22, 0.25, 0.27 nm) and traces of apatite (0.27, 0.34 nm) (Figure 2).

XRD patterns for the clay fraction show phosphate minerals as the main crystalline phases. The mineralogy was basically composed by leucophosphite (KFe₂(PO₄)₂(OH).2(H₂O)) (0.61, 0.55, 0.42, 0.28 nm), minyulite (KAl₂(PO₄)₂(OH,F).4(H₂O)) (0.55, 0.39, 0.34, 0.26 nm), fluorapatite (Ca₅(PO₄)F) (0.19, 0.26 nm) and apatite (Ca₁₀(PO₄)₆(OH₂)) (0.28, 0.26 nm) (Figures 3 and 4). The latter was the only mineral that occurred in all fractions, representing the primary bone-apatite from guano.

In addition, vermiculite (1.51, 0.86, 0.37 nm), plagioclase (0.24, 0.19 and 0.17 nm), augite (0.21, 0.24, 0.29 nm) and biotite (Figures 3 and 4) were also identified in the clay fractions, consistent with previous studies in Maritime Antarctica (Simas et al. 2007, Pereira et al. 2013, Rodrigues et al. 2019). Mica (biotite) has a nonexpendable d(001) of 1.04 nm, which is not affected by ethylene glycol solvation or heating (Figure 3). Strong 0.22 and 0.24 nm peaks (Figures 3 and 4) that remained stable after heating and glycerol solvation confirm biotite identification. Interestingly, these ornithogenic samples showed a presence of crystalline Fe-oxyhydroxides, remarkably, goethite (0.14, 0.15, 0.17, 0.22, 0.42 nm) (Figures 3 and 4), which is unusual for Antarctic soils (Simas et al. 2006). The DCB method was efficient for the removal of iron hydroxides.

Table II. Chemical properties of the ornithogenic soil pockets and reference samples from President Head Peninsula.

Sample	pH water	pH KCl	P	K	Na	Ca	Mg	Al	H+ Al	SB	cmolc.dm ³			PSB	Alsat	ISNa	OC	P-Rem
											CECeff	CECpot	%					
SP 1	5,0	4,6	6544,0	309,0	1044,0	8,4	3,4	0,2	12,2	17,2	17,4	29,4	58,4	1,2	15,5	9,6	46,4	
SP 2	4,8	3,8	3496,0	468,0	779,9	9,4	3,1	0,1	9,0	17,1	17,2	26,1	65,5	0,6	13,0	2,9	57,0	
SP 3	4,8	4,4	7072,0	209,0	1023,7	13,8	4,9	0,3	20,9	23,7	24,0	44,6	53,1	1,3	10,0	8,1	53,8	
SP 4	4,3	4,0	4557,9	289,0	1226,9	4,9	3,1	0,4	13,2	14,0	14,4	27,2	51,5	2,8	19,6	9,6	72,7	
SP 5	5,4	4,6	6355,4	209,0	1044,0	5,7	2,6	0,2	9,9	13,4	13,6	23,3	57,4	1,5	19,5	7,7	48,1	
SP 6	4,4	3,7	5159,8	249,0	495,4	7,8	2,0	0,6	12,5	12,6	13,1	25,1	50,1	4,5	8,6	11,7	48,7	
SP 7	5,3	4,4	5044,5	229,0	759,6	7,3	4,0	0,2	8,5	15,2	15,4	23,7	64,1	1,3	14,0	27,3	51,4	
SP 8	5,6	4,8	5377,5	368,0	1084,7	7,7	4,1	0,0	9,3	17,4	17,4	26,7	65,1	0,0	17,7	32,6	41,2	
SP 9	5,9	5,3	5652,2	151,0	718,9	11,4	6,7	0,0	11,1	21,5	21,5	32,6	66,0	0,0	9,6	8,3	28,4	
SP 10	5,8	5,2	6299,5	269,0	800,2	11,5	5,4	0,0	6,2	21,1	21,1	27,3	77,3	0,0	12,7	12,1	44,1	
SP 11	5,8	5,3	7092,1	249,0	434,4	8,9	2,2	0,0	5,2	13,6	13,6	18,8	72,3	0,0	10,1	9,4	48,7	
SP 12	4,7	3,8	3034,9	309,0	515,7	5,1	1,9	0,5	18,1	10,1	10,6	28,2	35,7	4,6	8,0	40,6	52,9	
SP 13	4,4	3,4	474,9	178,0	373,5	1,6	0,8	1,1	9,3	4,5	5,6	13,8	32,6	19,5	11,8	3,9	40,7	
SP 14	4,2	3,1	530,3	388,0	393,8	4,6	1,3	1,1	19,2	8,6	9,7	27,8	31,0	11,2	6,2	8,1	52,8	
SP 15	4,8	3,9	864,1	309,0	393,8	3,9	1,3	0,2	12,1	7,7	7,9	19,8	38,8	2,5	8,7	31,9	47,1	
Mean (n=15)	5,0	4,3	4503,7	278,9	739,2	7,5	3,1	0,3	11,8	14,5	14,8	26,3	54,6	3,4	12,3	14,9	48,9	
SD	0,6	0,7	2320,1	84,1	293,4	3,3	1,7	0,4	4,6	5,4	5,2	6,9	14,6	5,3	4,2	11,9	9,5	
Median	4,8	4,4	5159,8	269,0	759,6	7,7	3,1	0,2	11,1	14,0	14,4	26,7	57,4	1,3	11,8	9,6	48,7	
Non ornithogenic soil on marine terrace	4,1	4,1	118,8	124,0	820,0	3,7	3,0	1,6	9,7	10,7	12,3	20,4	52,3	13,2	17,5	7,8	12,2	
Non ornithogenic soil on plateau	6,0	4,1	50,7	134,0	380,0	5,2	3,6	0,6	3,6	10,8	11,3	14,4	74,9	5,0	11,5	2,6	31,7	

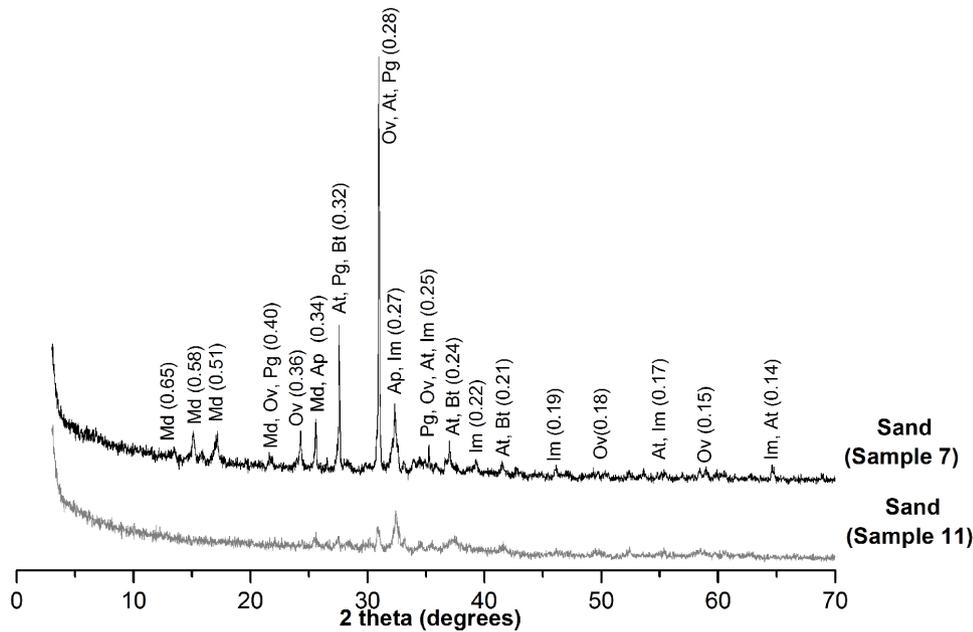


Figure 2. Representative XRD of sand samples of ornithogenic sites (samples 7 and 11).
 Md - mordenite; Ov - olivine; Bt - biotite; Pg - plagioclase; At - augite; Im - ilmenite; Ap - apatite). "d" in nm.

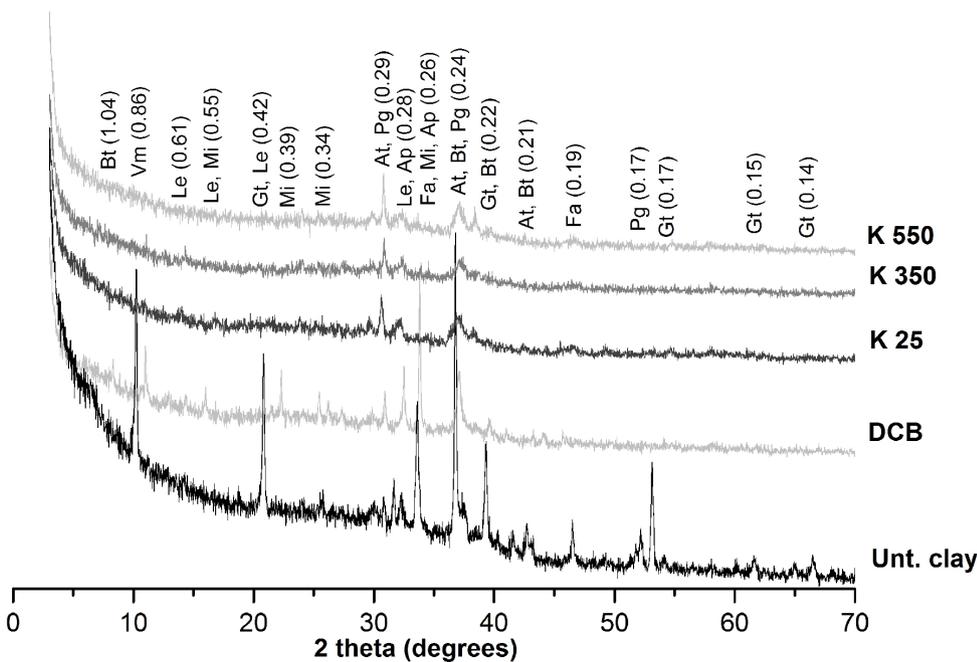


Figure 3. Representative XRD of clay sample of ornithogenic soil (sample 7).
 Unt. Clay - Untreated clay; DCB - removal of iron oxides; K - K⁺ saturation (heat treatment of K-saturated mounts to 25°, 350° and 550 °C). Vm - vermiculite; Bt - biotite; Pg - plagioclase; Le - leucophosphate; Mi - minyulite; Gt - goethite; At - augite; Fa - fluorapatite; Ap - apatite). "d" in nm.

Micromorphologically (Figure 5), the phosphatized soil pockets have well separated blocks and/or moderately separated planar microstructures. The groundmass consists of fragments of igneous rocks (andesitic basalts), feathers and bone apatite fragments as coarse material, immersed in a yellowish-brown P-rich

micromass, with a porphyric relative distribution. Coatings and infillings features are common within pores and around rock fragments. These features have a phosphatic composition, yellowish-red colors, crescent b-fabric, like those observed by Simas et al. (2007) on King George Island.

Table III. Descriptive statistics considering phosphatized sites affected by flying birds comparison with penguins.

Variables	Units	n	Mean	Median	Minimum	Maximum	Percentile	Percentile	Coef. Var.	Skewness	Kurtosis
							10.00000	90.00000			
Snow Island (flying birds)											
Silt	kg.kg	15	16.85	15.60	3.80	39.10	6.10	26.90	55.29	0.78	0.83
Clay	kg.kg	15	20.03	19.30	9.10	29.60	11.10	27.10	28.51	-0.27	-0.28
Sand	kg.kg	15	63.13	63.10	33.80	85.10	48.40	83.20	21.33	-0.30	0.35
pH water	-	15	5.00	4.83	4.16	5.90	4.27	5.83	11.78	0.18	-1.35
P	mg.dm ³	15	4503.67	5159.80	474.90	7092.10	530.30	7072.00	51.52	-0.81	-0.64
K	mg.dm ³	15	278.87	269.00	151.00	468.00	178.00	388.00	30.17	0.68	0.43
Na	mg.dm ³	15	739.23	759.60	373.50	1226.90	393.80	1084.70	39.68	0.17	-1.46
Ca	cmolc.dm ³	15	7.46	7.65	1.59	13.80	3.88	11.54	43.87	0.21	-0.27
Mg	cmolc.dm ³	15	3.11	3.06	0.82	6.65	1.28	5.42	53.44	0.65	-0.13
Al	cmolc.dm ³	15	0.32	0.20	0.00	1.09	0.00	1.09	110.97	1.36	1.11
H+ Al	cmolc.dm ³	15	11.78	11.10	5.20	20.90	6.20	19.20	38.65	0.76	-0.02
SB	cmolc.dm ³	15	14.49	13.99	4.49	23.69	7.66	21.52	37.22	-0.07	-0.46
CECpot	cmolc.dm ³	15	26.27	26.67	13.79	44.59	18.77	32.62	26.24	0.94	3.22
PSB	%	15	54.59	57.40	31.00	77.30	32.60	72.30	26.72	-0.33	-0.98
Al-sat	%	15	3.40	1.30	0.00	19.50	0.00	11.20	156.27	2.44	6.10
OC	dag.Kg	15	14.92	9.64	2.93	40.57	3.86	32.59	79.51	1.20	0.02
Penguin nesting areas in Antarctica*											
Silt	kg.kg	17	20.59	21.00	2.00	38.00	6.00	38.00	54.17	0.19	-0.91
Clay	kg.kg	17	15.76	15.00	4.00	39.00	5.00	32.00	57.33	1.25	1.82
Sand	kg.kg	17	63.65	62.00	24.00	93.00	42.00	85.00	28.49	-0.39	-0.15
pH water	-	17	5.41	5.31	4.20	6.72	4.61	6.59	13.36	0.30	-0.70
P	mg.dm ³	17	2636.14	819.90	174.70	8675.80	185.30	8326.50	125.83	1.09	-0.69
K	mg.dm ³	17	208.28	148.20	10.00	1134.90	74.00	347.10	120.97	3.45	13.08
Na	mg.dm ³	17	431.70	275.88	52.80	1269.00	117.10	1220.70	85.81	1.45	1.13
Ca	cmolc.dm ³	17	4.79	3.32	0.60	15.42	0.64	11.40	93.44	1.19	0.35
Mg	cmolc.dm ³	17	2.59	1.70	0.27	7.30	0.41	6.60	85.45	0.99	-0.17
Al	cmolc.dm ³	17	1.62	0.67	0.00	6.80	0.00	5.60	126.42	1.55	1.71
H+ Al	cmolc.dm ³	17	14.37	13.70	4.60	23.80	6.30	23.30	49.03	0.04	-1.78
SB	cmolc.dm ³	17	9.85	7.40	1.13	22.72	1.83	21.80	70.79	0.63	-0.89
CECpot	cmolc.dm ³	17	21.65	19.53	7.68	37.42	9.56	36.14	43.53	0.33	-1.06
PSB	%	17	40.15	39.20	4.80	83.20	9.40	72.20	58.12	0.23	-0.78
Alsat	%	17	20.95	6.00	0.00	72.80	0.00	71.10	123.88	1.07	-0.29
OC	dag.Kg	17	11.97	8.53	0.90	55.75	1.75	26.20	110.00	2.57	7.78

*Simas et al. (2007), Pereira et al. (2013), Simas et al. (2015) and Daher et al. (2019).

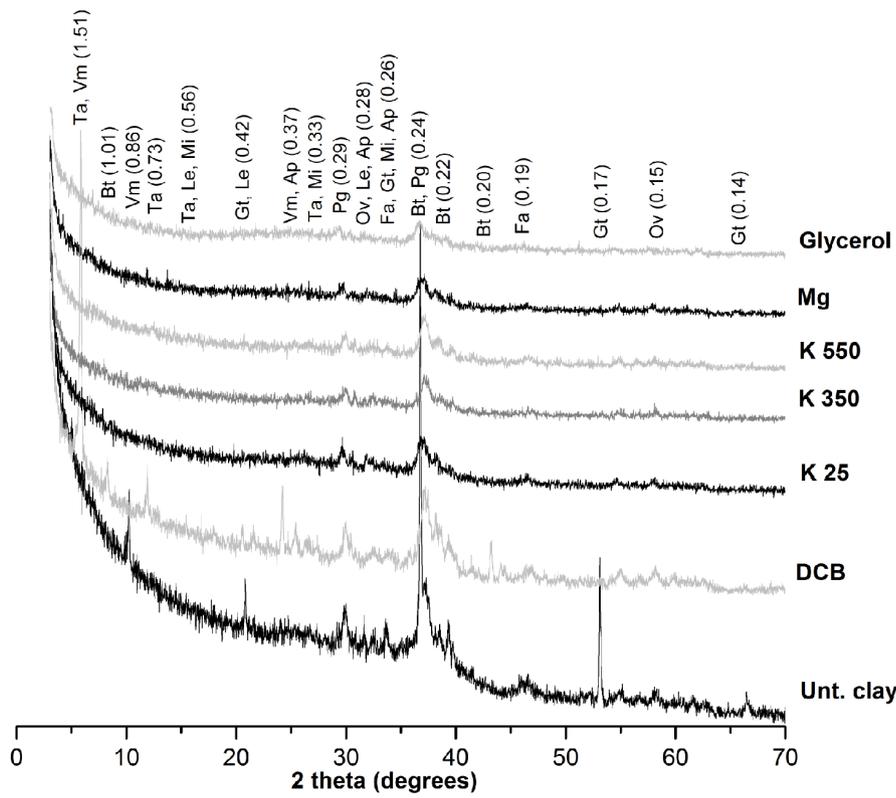


Figure 4. Representative XRD of clay sample of ornithogenic soil (sample 11). Unt. Clay - Untreated clay; DCB - removal of iron oxides; K - K⁺ saturation (heat treatment of K-saturated mounts to 25°, 350° and 550° C); Mg - Mg²⁺ saturation; Glycerol - saturated by Mg²⁺ and solvated by glycerol. Vm - vermiculite; Bt - biotite; Pg - plagioclase; Le - leucophosphate; Mi - minyulite; Gt - goethite; Fa - fluorapatite; Ov - olivine; Ap - apatite; Ta - taranakite. "d" in nm.

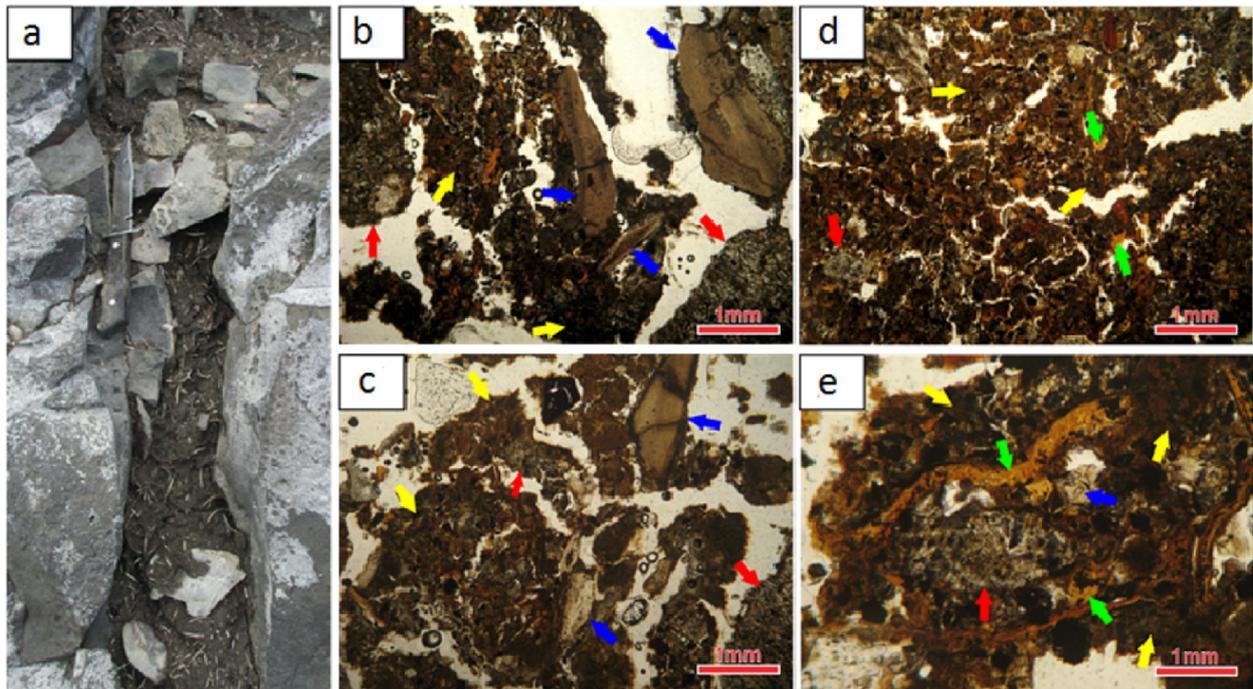


Figure 5. a) Macromorphological aspect and b, c, d, e) Micromorphological representative photomicrographs in ppl (parallel polarized light) of soil pockets affected by flying birds (phosphatized soils). Blue arrows indicate bone fragments. Red arrows indicate rock fragments. Yellow arrows indicate phosphatized micromass. Green arrows indicate amorphous iluvial Fe-P features.

DISCUSSION

Phosphatization flying bird's versus penguin's

The influence of penguins in soils from Antarctica seems to be spatially much greater than the influence of flying birds, but the potential capacity of phosphatization and chemical weathering in soils affected by flying birds compared with penguins is unknown.

The worldwide seabird population is estimated to be 804 million individuals (Otero et al. 2018), distributed mainly in the polar zones and oceanic islands, but concentrated in Antarctica and sub-Antarctic islands. The largest order is Procellariiformes, that comprises the family of petrels, with 424 million, followed by Charadriiformes, that comprises Stercorariidae/skuas with 291 million (Otero et al. 2018). These two birds are key species on rocky terrestrial environments in Antarctica.

The phosphatization is more intense in the southern hemisphere than the northern hemisphere, because differences in body masses and length of the breeding seasons produce greater nutrient excretions (Otero et al. 2018). An essential portion of the species present in Antarctica and its sub-Antarctic islands are large-sized and heavy weight (e.g. *Pygoscelis antarcticus*, 3–5 kg) (Otero et al. 2018). In PHP, the penguins soils showed the higher coefficient of variation (Table III) compared with soil pockets by flying birds, probably due to a greater dispersion of penguins at a single rookery, forming patches of different P concentration.

The maximum values of P and OC were recorded in penguin soils (8675.80 mg.dm³ and 55.75 dag.kg, respectively) (Table III). The breeding activity of penguins yields a key ecological effect at the coast zone of Maritime Antarctic (Tatur 2002) (Figures 6 and 7). The amount of daily dry excreta deposited by penguins on the land can be 46 higher than flying birds (Tatur 2002). In

Barrientos Island, Daher et al. (2019) reported a lower level of P in a soil pocket collected from an old giant petrel's nest, where the intensity of organic deposition was much lower compared with the active penguin soil from the vicinity.

Although the maximum values of P and OC were recorded in penguin soils, in our study the mean and median values of available P was higher in flying birds soil pockets (median of 5159.80 mg.dm³ of P and 9.64 dag.kg of OC) (Table III). These results can be explained by the concentrated of guano deposition in flying birds nests (locally hotspots for nutrients). Penguin activity leads to the formation of greater soil development in Antarctica with deep mixing of bird detritus and granular structure (Simas et al. 2007, Daher et al. 2019, Lopes et al. 2019). These conditions promote more deeper mobilization of guano horizontally and vertically compared to soil pockets by flying birds, where guano is sheltered in closed fractures and microdepressions, where leaching is reduced (Figure 6). In nunataks ecosystems of Antarctica, Cocks et al. (1999) reported the highest levels of nutrients were associated with the Petrel's nest itself, elevated levels still occurred at 1 m from the nest but dropped to levels similar to those of non-ornithogenic soils at 2 m or 5 m from the nest. Hence, our results have broad implications for understanding the importance of chemical weathering on rocky outcrops subjected to ornithogenesis in periglacial areas affected by flying birds.

Descriptive statistics demonstrate that soil pockets under flying birds activity show higher mean and median values of clay, P, K, Ca, Mg, BS, CEC, and OC compared to soils affected by penguin activity (Table III). The highest amount of nutrients in flying birds probably due the concentrated of guano deposition in microdepression relief on coastal outcrops (Figure 6). Chemical weathering is locally

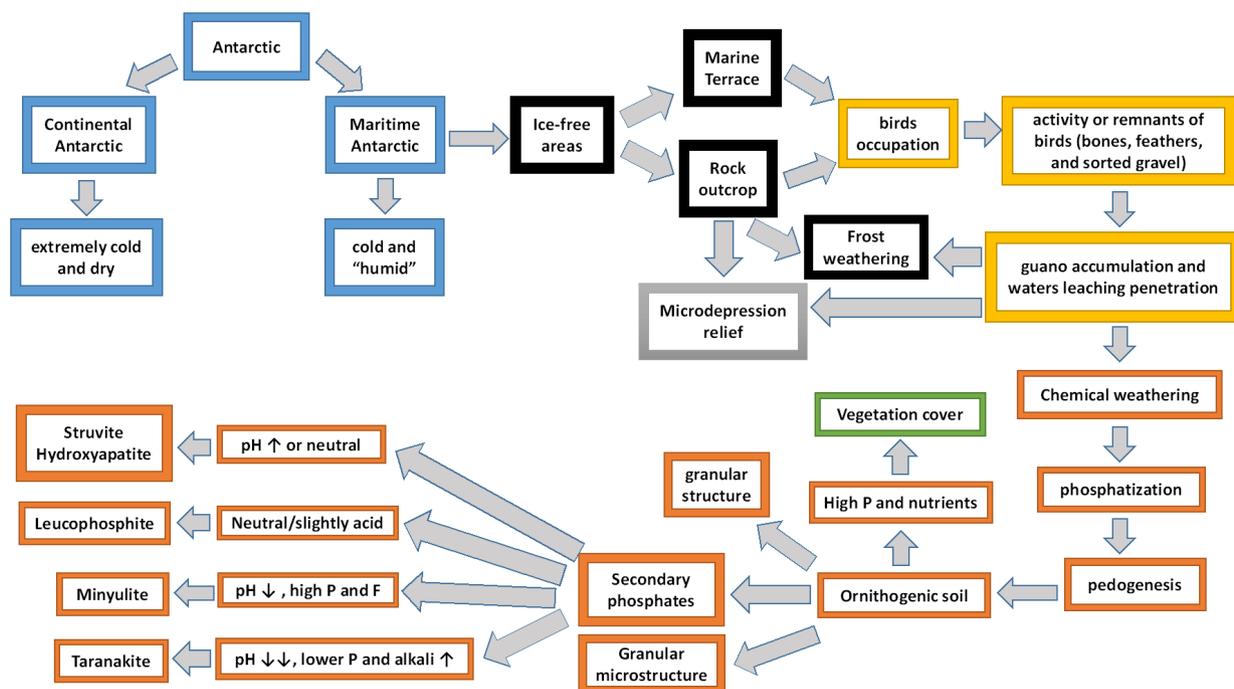


Figure 6. Integrated scheme of ornithogenic soil formation in Maritime Antarctica, the mineral assemblage representative of phosphatization and *pedoenvironmental* features. Blue color indicates association with climate conditions, black association with lithology, gray association with relief, yellow association with faunal activities, orange association with soil and green association with plants. Based on Tatur & Myrcha (1984), Simas et al. (2007), Schaefer et al. (2008) and Pereira et al. (2013).

impacted by concentrated guano addition (Lopes et al. 2021a), as can be confirmed by high clay content (median of 19.3 kg.kg) (Table III). In this regard, the clay content was the highest in more phosphatized and acid sites with the highest amounts of P in Barrientos Island, Antarctica (Daher et al. 2019).

The pH values on ornithogenic soils affected by penguins are similar to others reported from elsewhere in Maritime Antarctica (Michel et al. 2006, Simas et al. 2007, Pereira et al. 2013), with a mean of 5.41 (Table III), slightly higher than values reported in sites affected by flying birds in PHP, with mean of 5.00 (Table III). The statistical data demonstrated higher values Al, H+Al, and Al saturation for penguins soils. Guano is initially alkaline, but progressive acidification occurs, following the degradation of fresh guano (Pereira et al. 2013).

Flying bird’s phosphatization also contributes to soil mineralogical transformations

The PHP coastal outcrops are characterized by igneous volcanic rocks. X-ray diffraction patterns of the sand fraction show the presence of mordenite (usually found in andesite and basalt), olivine, biotite, plagioclase, augite, ilmenite, and traces of apatite (Figure 2). Lavas and hypabyssal intrusions are petrographically similar, aphyric rocks contain plagioclase (andesite), olivine (occurs only in the basalts and basaltic andesites), and augite (pyroxene mineral) at Snow Island (Smellie et al. 1984). Grains of ilmenite and rare apatite are described in the petrographic analysis presented by Smellie et al. (1984). Almost all igneous rocks contain apatite as phosphate as an accessory minerals (Nash 1984).

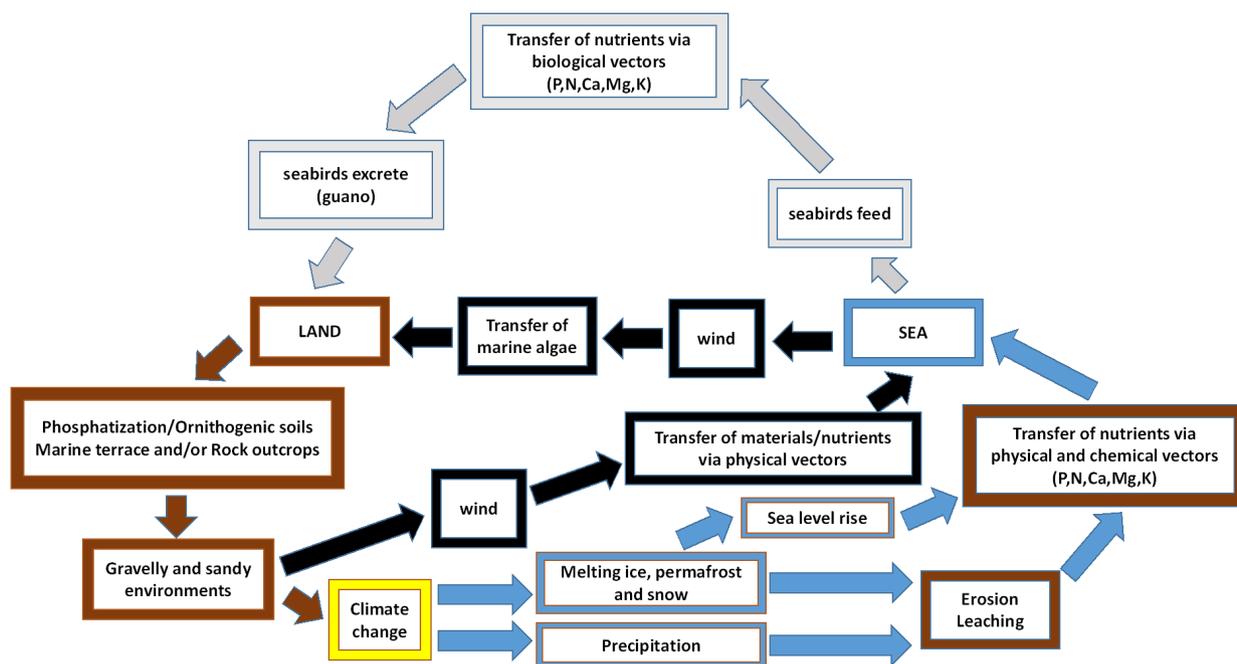


Figure 7. A proposal model of sea-land nutrient transfer in Maritime Antarctica, using climate change scenario, biological, physical and chemical vectors. Blue color indicates association with water, black association wind, gray association with seabirds, yellow association with climate and brown association with land. Informations extraction from Simas et al. (2007), Qin et al. (2014), Schaefer et al. (2017) and Otero et al. (2018).

In soil-rock contact zone, phosphatization leads to intense alteration of the lithomargin, resulting in the neoformation of phosphatization products *in situ*, as secondary minerals, although fragments of unaltered minerals are preserved (Tatur & Myrcha 1984) (Figure 5). Preserved minerals in rock fragments are also observed in Snow Island by minerals like olivine, plagioclase, and biotite. In the studie soil pockets from Snow Island, we found a mixture of three phosphates with silicates in every sample. The presence of different phosphates proves varying physical and chemical conditions during phosphatization (Tatur & Myrcha, 1984).

The phosphate assemblage on Snow Island includes leucophosphite, minyulite, fluorapatite, and apatite, confirming a highly active chemical weathering environment, by input by flying birds (Figure 6). A mineral assemblage representative of phosphatization was reported in several

recent studies in coastal areas of Antarctica, but always associated with penguin activity (Tatur & Myrcha 1984, Simas et al. 2007, Schaefer et al. 2008, Pereira et al. 2013). Slight differences may occur regarding the formation and degradation of particular phosphate minerals like the geochemical nature of the parent rock, parent rock porosity, and local landforms (Flicoteaux & Lucas 1984) (Figure 6).

The most important phosphate in the guano layer is hydroxyapatite, besides struvite (magnesium ammonium phosphate), the latter commonly precipitated from concentrated solutions, both are stable minerals under neutral or alkaline reaction of soils (Tatur & Myrcha 1984) (Figure 6). Struvite was not detected in Snow Island, where ornithogenic soil pockets have an acidic reaction with pH (water) ranging from 4.2 to 5.9 (Table II). Confirming this pattern, struvite was detected in soils from Hope Bay,

Antarctic Peninsula, semiarid soils, with slow degradation of organic compounds and higher mean pH value of 6.1 (Pereira et al. 2013).

Once guano deposition occurs, the ornithogenic P is expected to react first with amorphous aluminosilicates due to their large surface area and high P affinity (Simas et al. 2007). Soils of the South Shetland Islands are considered weakly developed, and chemical weathering processes are considered to be reduced, except in ornithogenic environments (Haus et al. 2016). The presence of weatherable primary minerals (such as plagioclases detected in the clay fraction) and secondary minerals (such as phosphates and iron hydroxides) (Figures 3 and 4) indicate that chemical weathering is not advanced in these soils at the coastal zones of Antarctica. Soil acidification favors the transformation of weatherable mafic minerals and releases highly reactive, amorphous Al/Fe minerals, which further react with ornithogenic P to form amorphous and crystalline Al/Fe-phosphate minerals (Simas et al. 2007) (Figure 5).

Ornithogenic environment and impacts of the phosphatization processes

The ornithogenic environment can be considered a natural landscape unit and exhibits well-defined attributes (Figure 7), significantly distinct from the surrounding areas. The comparison of morphological, physical, chemical, and mineralogical properties between non-ornithogenic and ornithogenic soils allows a better understanding of the impacts of the faunal activity on the Antarctic terrestrial ecosystems (Simas et al. 2007).

Phosphorus from seabirds guano influences the terrestrial and freshwater ecosystems of Antarctica (Qin et al. 2014). Fresh feces, under the influence of melting and rains, are partly washed back to sea, but leachates of guano interact with the coarse soil matrix, forming a broad zone of

phosphatization (Tatur & Myrcha 1984, Lopes et al. 2021a) (Figure 7). In Snow Island, the zone of phosphatization has higher concentration of P (37.9 times higher than non-ornithogenic soils on the marine terrace), K (2.2 times higher), and Ca (2.0 times higher) (Table II). Clay values are 1.65 higher than non-ornithogenic soils (Table I), suggesting an association between clay formation and chemical weathering promoted by the phosphatization process.

Guano deposits contain phosphates and oxalic acid, causing phosphatization and/or dissolution of silicates (Haus et al. 2016) (Figure 6). A layer of mineralized guano, rich in calcium phosphates, occurs in these areas (Tatur & Myrcha 1989, Lopes et al. 2021a). The mean pH for the ornithogenic soils studied in the present work is 5.0, which is lower than the mean pH of the non-ornithogenic soils on the plateau (6.0) (Table II).

In Antarctica, high amounts of organic matter is only accumulated in coastal ornithogenic soils (Tatur & Myrcha 1989). In the present study, organic carbon is 5.7 times higher than non-ornithogenic soils on the plateau. The high concentration of P, K, Ca, and organic matter favors vegetation development in ornithogenic soils at Maritime Antarctica (Simas et al. 2007, Daher et al. 2019, Lopes et al. 2019) (Figure 6). Otero et al. (2018) estimated worldwide fluxes of total nitrogen (N) and total phosphorus (P) excreted by seabirds to be 591 Gg N y^{-1} and 99 Gg P y^{-1} , with the Antarctic and Southern coasts receiving the highest N and P inputs.

High levels of Na^+ in ornithogenic soils (mean 739.2 mg dm^{-3}) are attributed to salt-sprays brought by winds (Daher et al. 2019). Na^+ levels in non-ornithogenic soils increased downslope from the plateau (380.0 mg dm^{-3}) to the coastal non-ornithogenic soil on the marine terrace (820.0 mg dm^{-3}) (Table II).

Landforms regulate drainage and surface slope stability and change the nature or concentration of percolating solutions (Flicoteaux & Lucas 1984). The rocky outcrops landforms at Antarctic coastal areas are very relevant for understanding the microscale of phosphatization processes. Chemical alteration is especially intense when guano is sheltered in closed fractures and depressions, where leaching is reduced (Figure 6). Thereby, a permanent and intense reation phosphatization occur. The phosphatization occurs most efficiently in deeper layers, notably in stony and permeable material (Tatur & Myrcha 1984), subjected to physical breaking by freezing-thawing.

Faunal activity in coastal areas in Antarctica can induce permafrost degradation and enhanced periglacial erosion, as reported by Schaefer et al. (2017). Areas that receive large additions of seabird guano in Snow Island, in soil with high contents of gravel and sand (Table I) are prone to high erosion rates (Figure 7). Taking the above into account, global warming can remobilize nutrients stocked in ornithogenic environments returning them to the sea, by increasing erosion due to permafrost thawing and sea-level rise (Figure 7), as well as to a presumable increase in pluvial precipitation in Antarctic or sub-Antarctic ecosystems (Otero et al. 2018).

CONCLUSIONS

1. This study demonstrates that even under typical periglacial conditions in Antarctica, local, small soil pockets influenced by flying birds present active chemical weathering processes, such as phosphatization, and high chemical fertility.

2. The phosphatization is a chemical processes that release exchangeable

bases and accelerate mineralogical and micromorphological transformations in soils, even under periglacial conditions. Despite their reduced geographic extension, these sites are important hotspots of nutrients and vegetation micro-oasis in Antarctic terrestrial ecosystems.

3. Phosphatization is a key soil-forming process in Antarctic terrestrial ecosystem resulting in changing chemical (nutritional). Formation of secondary minerals in soil pockets at Snow Island result from unusual chemical weathering processes.

4. Flying seabirds are one of the main factors influencing the vegetation establishment in rocky outcrops in Maritime Antarctica.

5. Under the current global warming trend and expected sea-level rise, the ornithogenic environments of Snow Island are susceptible to accelerated erosion rates and a great part of these hotspots may be lost for the open sea.

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