An Acad Bras Cienc (2024) 96(Suppl. 2): e20230529 DOI 10.1590/0001-3765202420230529
Anais da Academia Brasileira de Ciências | *Annals of the Brazilian Academy of Sciences*
Printed ISSN 0001-3765 I Online ISSN 1678-2690
www.scielo.br/aabc | www.fb.com/aabcjournal

SOIL SCIENCE

Contribution by Giant petrels and Brown skuas to soil phosphatization in Harmony Point - Maritime Antarctica

WILLIAM F. RODRIGUES, FÁBIO S. DE OLIVEIRA, CARLOS ERNESTO G.R. SCHAEFER, MARIÂNGELA G.P. LEITE & ISABELA C. TORRES

Abstract: This research was conducted for the purpose to evaluate the contribution Giant petrels and Brown skuas nestings in the formation of ornithogenic soils by the phosphatization process in Harmony Point, Maritime Antarctic. Ten nests were selected to collect topsoil samples (0-20 cm), from 0 m up to 20 m away, with regular spacing of 2 m. The analysis of the samples included the physical, chemical, mineralogical and geochemical analyzes. Phosphate minerals were identified. The presence of high content of some trace elements, such as Zn, Cu and Sr is associated with the bird's excrements. Total-P and bioavailable-P recorded higher levels. This result demonstrates the importance of the time factor in the bird's nesting, as well as in the development of the soil in these soil-forming environment. Phosphatization in these areas is not restricted to the specific location of the nest, since high values of P have been identified at distances between 8 and 12 m, from de nest's top. This suggests the transport of P rich solutions and phosphatized material along fractures by the freeze-thaw cycles, contributing to increase the geographical expression of this phenomenon in this ice-free area, consequently the development of soils and the establishment of vegetation.

Key words: Ornithogenic soils, Nests of Giant petrels and Brown skuas, Non-penguin nidification, Nelson Island.

INTRODUCTION

Maritime Antarctica compared to Continental Antarctica has higher temperatures and greater availability of water, what favors the establishment of bird colonies (Campbell & Claridge 1987, Simas et al. 2007). These colonies are important in island ecosystems, including the South Shetland Island (SSI) (Tatur & Barczuk 1985, Simas et al. 2007).

During the austral summer, guano accumulation from birdlife represents one of the largest sources of organic matter (Ugolini 1972). The decomposition of this organic matter enhances chemical weathering and phosphatization. The bird's colonization time, the intensity of guano deposition, the characteristics of the substrate and the climatic conditions are important factors to drive the phosphatization process (Tatur & Myrcha 1993). Phosphatization in nesting areas is able to development the ornithogenic soils (Ryan & Watkins 1989, Signa et al. 2012, Gagnon et al. 2013).

Studies of genesis of ornithogenic soils in Maritime Antarctic have pointed out that these soils are the most developed soils for the Antarctica context, due to some characteristics as higher clay contents, greater performance of chemical weathering and consequently, a good development and stabilization of vegetation in the places where these soils form (Michel et al. 2006, 2014, Simas et al. 2007, 2008, 2015, Francelino et al. 2011, Moura et al. 2012, Poelking et al. 2015, Rodrigues et al. 2019).

The phosphorus enrichment in soils by guano birds has been recognized as one of the most important pedogenic processes in Maritime Antarctica (Tatur & Myrcha 1989, Myrcha & Tatur 1991, Schaefer et al. 2004, 2008, Michel et al. 2006, Simas et al. 2007, 2008, Pereira et al. 2013). Thus, ornithogenic soils may be associated with present or former nests, mainly penguins, with varied degree of development and mineral phosphate content (Rakusa-Suszczewski 1993).

SSI are nesting areas not only for penguins, but also for other birds, especially Diomedeidae families (albatrosses), Procellariidae and Hydrobatidae (petrels), Phalacrocoracidae (cormorants), Stercorariida (B. skuas), Laridae (swallows), and others (Clements et al. 2017). These birds have slightly different behavior. In addition to coastal areas, they can become established in the inner of islands and occupy rocky outcrops, crests and intermediate plateaus (Silva et al. 1998). Harmony Point in Nelson Island, proves to be a favorable habitat for seabird occupation, like Southern Giant Petrel *Macronectes giganteus* and Brown skua *(Stercorarius antarcticus* ssp.) (Silva et al. 1998, Krüger 2019). Although phosphatization is important in Maritime Antarctica terrestrial ecosystems, the contribution of birds in smaller colonization compared to penguins to the phosphating process is still not well known.

In this sense, this study focuses on evaluating the phosphatization by Giant Petrels (G. petrels) and Brown B. skuas (B. skuas), due to the concentrations of these birds in some locations on the island (felsenmeers), leading to the following question “are these birds with smaller size and lesser number of nests than penguin colonies able to contribute to the phosphatization process in soils?”

Thus, the aims of this study were (i) to measure the geochemical phosphorus background in areas containing G. petrels and B. skua’s nests; (ii) to evaluate, based on geochemical and mineralogical indicators, the role of these birds in the formation of ornithogenic soils, and (iii) to compare our results with those in penguin rookeries.

MATERIALS AND METHODS

Study area

Harmony Point - Nelson Island is located in the South Shetland Island (SSI) selected (Fig. 1). This area has approximately 4 km^2 and is recognized as an Antarctica Specially Protected Area (Number 133) due to the presence of great diversity of birds.

Studies in the SSI suggest that the islands have been affected by two glaciations, one during the middle Pleistocene and another in the late Holocene (post-5 ka B.P.) (John & Sugden 1971, Clapperton & Sugden 1988). Thus, most of the present ice-free areas at Harmony Point were covered during the last Quaternary glaciation (Pallàs et al. 1995). The main Geological features are tuffs and andesitic basalts (Smellie et al. 1984). There are also micro-gabbro intrusions southwest of the area (Smellie et al. 1984).

The geomorphological constitution occurred mainly after glacier retreat due to the increase of the average temperature of the Maritime Antarctica (López-Martínez et al. 2012), the area was subjected to paraglacial and periglacial processes, leading to the establishment of permafrost in some landscape positions. As a result, glacio-isostatic compensation contributed to the formation of a coastal domain with sunken beaches, today marine terraces that are interspersed with stacks and rocky outcrops. In the upper platform, is subdivided into cryoplanated surfaces, with *in situ* cryoclastic

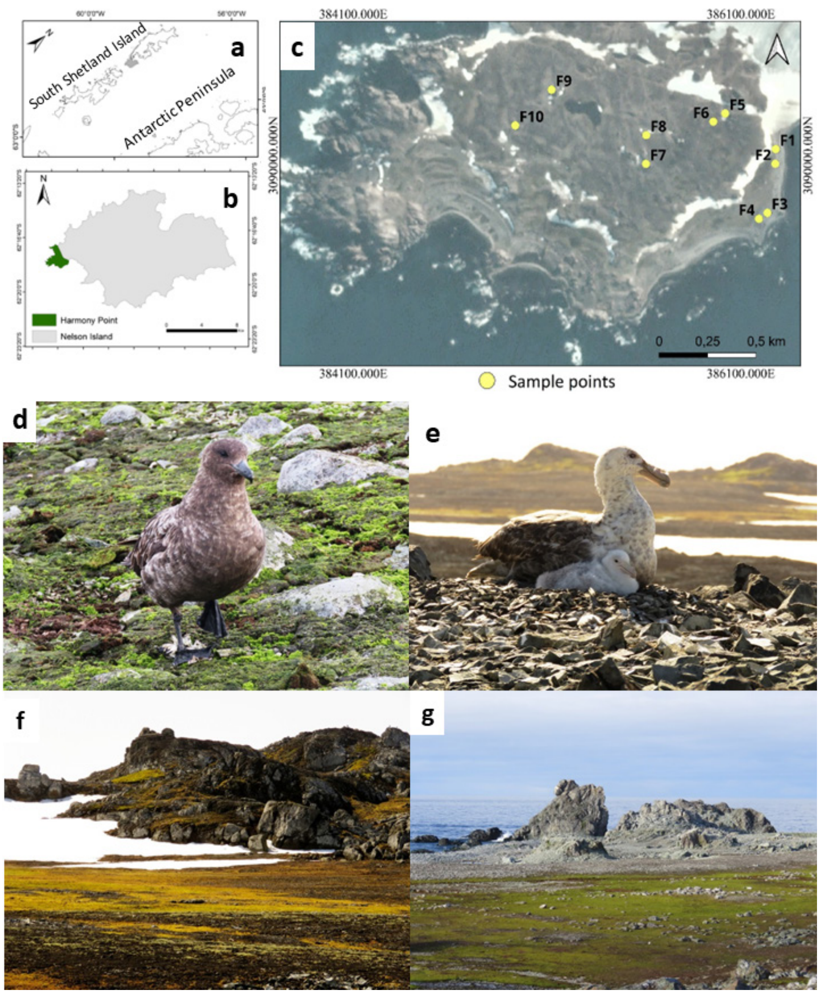

Figure 1. Location of Harmony Point, Nelson Island, Maritime Antarctica, with the respective nests under study. a: South Shetland Island; b: Nelson Island; c: Harmony Point and the samples location; d: G. Petrels nest's; e: B. Skua; f: Felsenmeers at cryoplanated plataform; g: Outcrops in marine terrace (coastal domain).

rock fragment fields, also called felsenmeers (French 2007). These geomorphic unities are preferred nesting sites for these birds.

The weather station closet to Harmony Point is 17 km away, on the Fildes Peninsula on King George Island (2000- 2012, Lieutenant Rodolfo Marsh Martin Aerodrome and Meteorological Station) where the average annual temperature is -2.2 °C and summer precipitation ranges from 350 to 500 mm (Øvstedal & Lewis Smith 2001).

The vegetation is composed of a diverse community of bryophytes and lichens, with extensive moss areas at some higher terrace positions and in the flooded depressions on the upper platform (Ochyra et al. 2008). Felsenmeers have unusually diverse types of lichens and mosses (Olech 2004).

Harmony Point has a good diversity of seabirds, approximately 12 species (Silva et al. 1998). Concentrating a total of 481 active nests (Krüger 2019). Of the largest numbers of species, Gentoo Penguin *Pygoscelis papua* (1230 pairs), Chinstrap Penguin *P. antarctica* (5205 pairs), Southern Giant Petrel *Macronectes giganteus* (56 pairs) and Brown skua *(Stercorarius antarcticus ssp*) (61 pairs) (Silva et al. 1998).

Soils at Harmony Point are particularly influenced by the parent materials, variations in climate at different elevations, landform age, and biota. Rodrigues et al. (2019) recognized three soil orders at Harmony Point (Gelisols, Entisols, and Inceptisols) and five suborders (Orthents, Orthels, Turbels, Histels, and Gelepts) (Soil Survey Staff 2014). In addition to cryoturbation, phosphatization may be considered one of the main pedogenic processes at Harmony Point, considering that 70% of soils investigated by Rodrigues et al. (2019) were affected by penguin activity. The remarkable presence of ornithogenic soils in this ice-free area of the SSI was one of the motivators for the conduction of this study.

Soils sampling

The fieldwork was carried out in the southern summer between February and March in 2015. Ten nests occupied by G. petrels or B. skuas in coastal domain (marine terrace MT) and cryoplanated platform (CP) domains were selected for this study (Fig. 1d, e, f, g). Four of them (F1 to F4) are located on the marine terrace, on the top of rocky outcrops stacks (Fig. 1g). F1 and F2 are located on the second terrace, and F3 and F4 are closer to the current beach (Fig. 1g). The others (F5 to F10) are located in the eastern portion of the cryoplanated platform (CP), always on the top of felsenmeers (Fig. 1f). In each nest, systematic collections of topsoils (0-20 cm) were performed at regular interval of 2 m up to 20 m (Fig. 2), totaling 110 samples.

Chemical, physical, mineralogical and statistical analyses

Soil texture was analyzed by mechanical dispersion of < 2 mm in distilled water, sieving and weighting of the coarse and fine sand, sedimentation of the silt fraction followed by siphoning of < 2 μm fraction (Gee & Bauder 1986). All routine analytical chemical and physical determinations were obtained using standard procedures (EMBRAPA 2017). Soil pH (determined in 1:10 soil/water solution) and exchangeable nutrients were determined for < 2 mm air-dried samples (EMBRAPA 2017). Mg^{+2} and Al^{+3} were extracted with 1 mol L^{-1} KCl and P, Na and K were extracted with Melich-1 (EMBRAPA 2017). Element concentrations in extracts were determined by atomic absorption (Ca^{+2}, Mg^{+2} and Al^{+3}), flame emission (K and Na) and photocolorimetry (P) (Murphy & Riley 1962). Organic matter was determined by wet combustion (Yeomans & Bremner 1988). Total nitrogen was determined by Kjeldahl method (EMBRAPA 2017).

Major and trace elements (Al, Fe, Ca, Mg, Na, P, Ti, K, Mn, Ba, Cr, Cu, Li, Zn, Sr, V, Y, Sc) were determined using the method proposed by Moutte (1990), including triacid attack: HNO_3 (10 mol/l), HCl (10 mol/l) and concentrated HF, with

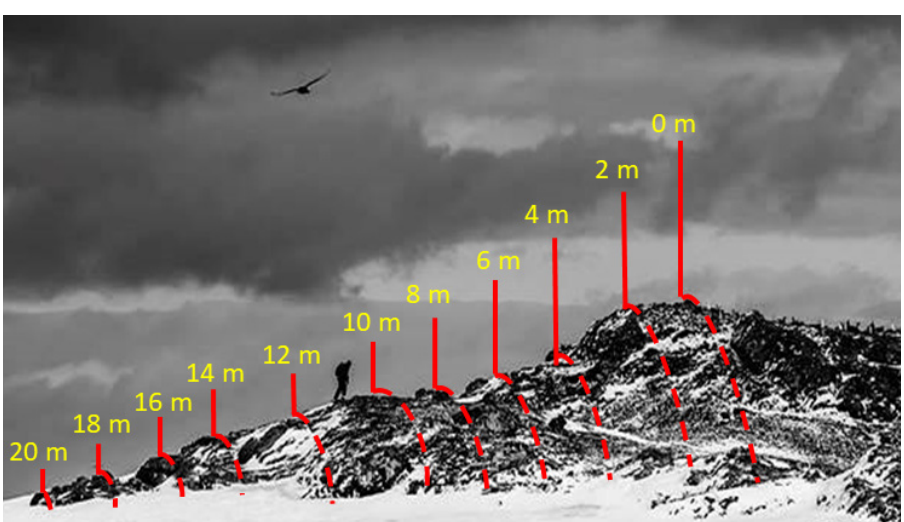

Figure 2. Felsenmeer (F9 sample) illustrating the sampling performed. The collection interval was 2 m up to the limit of 20 m. Sample 0 m corresponds to the nest. Photo: Ricardo Leizer.

ICP–OES (Inductively Coupled Plasma Optical Emission Spectrometry) detection.

About 0.5 g of clay fraction for selected samples had mineralogy evaluated by X-ray diffraction (PANalytical X'Pert PRO diffractometer, with CoKα radiation, scanning in the range from 4 to 50° 2θ). Minerals were identified in High Score Plus Program and according Brindley & Brown (1980).

Statistical analyses

In this study, statistical analyses were carried out in two statistical softwares: SPSS 17 and MNITAB 16. The normality of the data was evaluated using a Kolmogorov–Smirnov (K–S) test. As data were not normally distributed, a non-parametric version of the ANOVA was used to test the significance of differences between data subsets. The Kruskal–Wallis (K-T) test was performed to define whether there was a significant difference between soil elemental concentrations among the two geomorfic units (MT and CP). The K–W test was also carried out to exam the significant differences in elemental concentrations among the distances from the nests. For all statistical analyses, two significance levels were considered: $\alpha \leq 0.05$ and $\alpha \leq 0.1$.

RESULTS AND DISCUSSION

Physical and chemical topsoil's properties

The coarse sand fraction (2-1 mm) are predominant in the marine terrace (MT) (mean of 47.3 %), and clay (19.5 %), in the cryoplatanetd plarform (CP) (Table I).

The topsoils are acidic, with mean pH of 4.8 for both domains (Table I). The pH values are similar to those reported for ornithogenic soils in area with penguin activity (Simas et al. 2007, Mendonça et al. 2013). These values can reflect the presence of acids, such as HNO_3, produced from guano decomposition (Tatur & Barczuk 1985).

Exchangeable Ca^{2+}, Na^{+}, K^{+} and Mg^{2+} is greater in soils from the MT (Table I). Tatur & Myrcha (1993) associated the enrichment in such elements to the deposition of urates, resulting from recent activities of seabirds.

Table I. Descriptive statistics of the main soil properties for sampling point from marine terrace and cryoplanated platform (n= 44 marine terrace; n= 66 cryoplanated platform).

	Marine terrace (MT)					Cryoplanated platform (CP)				
Variable	**Mean**	**SD**	**CV%**	**Max**	**Min**	**Mean**	**SD**	**CV%**	**Max**	**Min**
pH	4.8	0.8	16.3	3.8	6.6	4.8	0.6	13.0	3.8	6.0
P(mg/dm^3)	2335.0	1708.0	73.2	200.0	6972.0	1098.5	744.2	67.7	41.9	3848.1
K(cmol$_c$/kg)	0.6	0.3	53.6	0.2	1.3	0.3	0.1	36.6	0.1	0.7
Na(cmol$_c$/kg)	2.2	1.4	65.6	0.4	5.5	0.8	0.3	36.1	0.1	2.0
Ca^{2+} (cmol$_c$/dm^3)	6.0	4.1	67.8	1.0	18.6	1.6	1.0	63.9	0.5	4.8
Mg^{2+}(cmol$_c$/dm^3)	2.8	1.4	48.2	0.5	6.7	0.6	0.4	57.3	0.2	1.6
Al^3(cmol$_c$/dm^3)	1.6	2.2	140.6	0.0	11.3	1.9	0.9	45.8	0.4	3.5
COT	1.4	0.6	44.9	0.4	2.8	3.8	1.6	40.8	0.7	6.4
N-total %	0.6	0.1	16.6	0.2	0.8	0.5	0.1	29.2	0.3	0.8
Coarse sand%	47.4	23.8	50.3	83.4	21.5	33.4	9.1	27.1	57.7	19.9
Fine sand%	11.0	9.8	88.7	42.3	3.2	24.9	8.6	34.6	46.1	7.3
Silt%	14.4	9.3	64.3	39.6	3.0	20.6	6.1	29.7	36.9	11.0
Clay%	15.8	7.3	46.0	26.7	9.6	19.5	5.2	26.4	30.9	11.0

Al^{3+} values are slightly higher on the CP. Several authors, such as Schaefer et al. (2004), Michel et al. (2006) and Simas et al. (2007), emphasized that aluminum content is related to the pedogenic development degree of ornithogenic soils.

All soils have high Na levels, ranging from 452 mg/dm^3 to 1255 mg/dm^3. The highest values were identified on marine terraces (Fig. 3).

The greater variation in Na content in the coastal domain suggests that its accumulation occurs irregularly, depending mainly on the influence of the marine spray, justifying the high values in nests located in volcanic stacks of the coastal domain, in direct contact with the sea (Navas et al. 2008, Simas et al. 2007). Although less important, Na content is also related on the presence of Na-rich minerals (Groeneweg & Beunk 1992). According to Pride et al. (1990), these two elements are that best reflect the presence of soluble salts, common in environments under the influence of marine spray (Sheppard et al. 2000).

Values of bioavailable-P, range 41.9 mg/dm^3 to 6972 mg/dm^3. The P distribution along the 20 m transect for both domains is shown in Fig. 4. In turn, bioavailable-P shows greater difference between domains. In this case, the MT presents values higher compared to CP.

As suggested by Simas et al. (2007), the identification of ornithogenic soil includes the presence of some attributes, especially bioavailable-P values higher than 500 mg/dm^3 extracted by Melich-1 and presence of current or past nesting signals such as feathers, bones, egg shells, shells, fragments of rocks aligned and selected, etc. All of these evidences are confirmed in the areas nested by G. petrels and B. skuas. In nests under study, the mean bioavailable-P was 1612 mg/dm^3, higher than found for ornithogenic soils in areas of penguin activity in the same area (Rodrigues et al. 2019), which is 1385 mg/dm^3.

Organic matter (OM) content is lower in the MT (2.4 dag/kg, on average), compared to the CP (6.6 dag/kg, on average). Low organic matter values in areas near the sea were also reported by

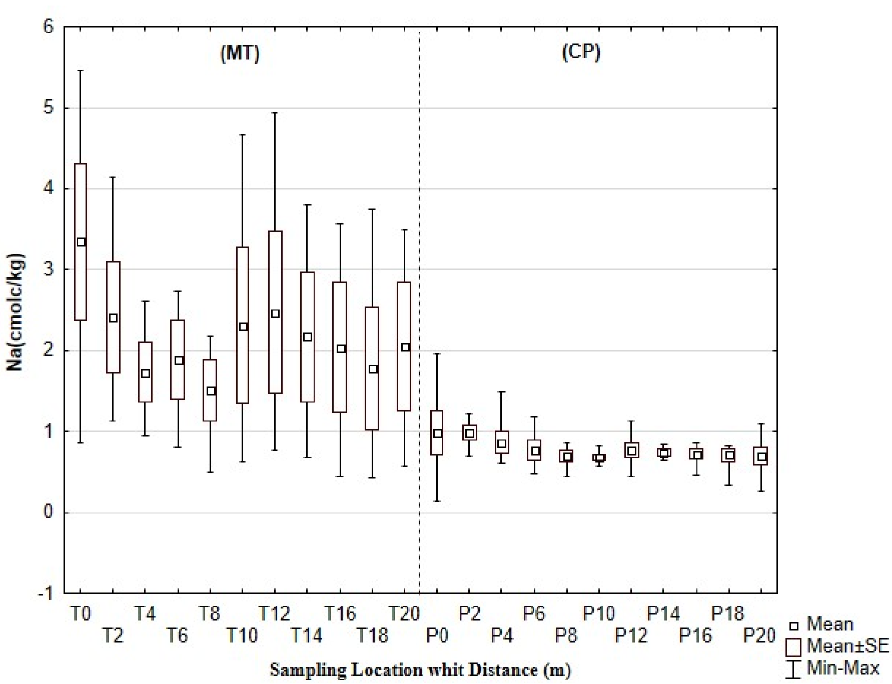

Figure 3. Box-Plot (with mean, standard deviation and minimum and maximum values) of Na content in soils collected from Coastal and Platform domains.

Navas et al. (2008) in Hurd and Byers Peninsula. The OM content may be related to the intensity and evolutionary ornithogenesis degree, where the low concentration suggests recent origin of organic matter (Beyer et al. 1997). However, these values also reflect the contribution of higher or lower vegetal cover density. Older ornithogenic soils may have provided better conditions for the establishment of mixed communities and, therefore, present higher concentrations. Low OM values in Maritime Antarctica soils are commonly associated with higher declivity sites, intense erosion and less pedogenesis rate (Carvalho et al. 2013), characteristic conditions of areas nested by these species in the study area. Regardless of the amount, accumulated organic matter plays an important ecological role (Beyer et al. 1995, Beyer 2000, Bölter & Kandeler 2004, Simas et al. 2008).

The total N contents ranged from 0.24 to 0.75 dag/kg, with slightly higher averages for the MT. In soils with high P concentrations, higher organic matter and nitrogen values are expected, associated with guano in the form of chitin and uric acids (Pietr et al. 1983). However, high values are commonly estimated for soils with great influence of penguins, due to the greater guano contribution in these sites. A large proportion of the nutrients concentrated in ornithogenic soils are a consequence of bird diet (Tatur & Myrcha 1989, Schaefer et al. 2004, 2008, Michel et al. 2006, Simas et al. 2007). Like penguins, G. petrels and B. skuas present diet based on fish and eggs, which makes their excrement also enriched in P and N (Hutchinson 1950).

Mineralogy

The mineralogical composition of soils shows the presence of plagioclase feldspar (andesine and anorthite) and phyllosilicates, such as expansive clay minerals (vermiculite and montmorillonite), chlorite and micas (paragonite, muscovite and biotite), as well as pyroxenes, quartz, and calcite in few samples. There were also zeolites, kaolinite, and phosphate minerals such as apatite, leucophosphite (Fig. 5) and vivianite.

Quartz peaks were identified in the clay fraction of soils from some nests. The presence

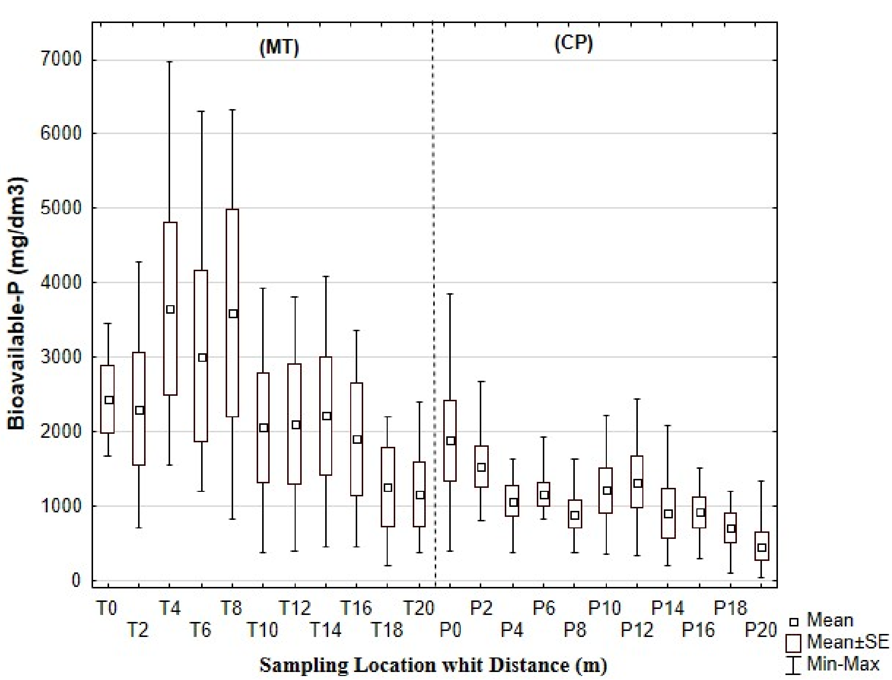

Figure 4. Box-Plot (with mean, standard deviation and minimum and maximum values) of bioavailable-P content in soils collected in the marine terrace (MT) and Cryoplanated Platform (CP) in relation to the distance from nests (numbers in meters).

of quartz in the clay fraction is attributed to cryoclastic weathering (French & Guglielmin 2000). Calcite was identified in three nests samples, and may be related to the amount of material used by birds to cover their nests, such, feathers, prey remnants, and egg shells (Polis & Hurd 1996), as well as calcite weathering (Navas et al. 2008). Hydrothermal influence on rocks from SSI resulted in their carbonation through the formation of calcite veins, common in the outcrops of several islands (Smellie et al. 1984).

Zeolite was abundant in the MT samples. According to Navas et al. (2008), zeolites have authigenic origin and their presence in Antartic soils is related to the weathering of volcanic rocks, mainly by the fragmentation of cavities (amygdala) filled by them.

The presence of kaolinite was detected and this, in the context of Antarctica soils, has been attributed to the parental material (Jeong et al. 2004) or to the weathering of feldspars and micas due to good drainage conditions (Bockheim 1980) or acidification in sulfated soils (Simas et al. 2006).

The mineral assemblage found in nest samples and their association with the parent material indicates the strong cryoclastic weathering action weathering in stacks and felsenmeers areas. When fragmented into clays, these minerals do not show conditions of advanced chemical weathering.

The presence of primary feldspars and phyllosilicates in the clay fraction is common in soils of SSI, which has been attributed to the important role of *in situ* physical weathering by cryoclastic processes (Simas et al. 2006, 2008), glacial comminution (Jeong et al. 2004), and wind deposition of volcanic ashes (Lee et al. 2004). At Harmony Point, soil material (lavas and andesitic tuffs) explains its presence. Many of these tuffs have greenish color, evidencing the presence of chlorite (Jeong & Yoon 2001), which was identified in the clay fraction.

In the case of vermiculites and montmorillonites in Antarctica soils, there is a controversy about their source, if is from diagenetic origin (Srivastava et al. 2011, Jeong & Yoon 2001, Lee et al. 2004, Simas et al. 2006) or by the weathering of primary phyllosilicates and

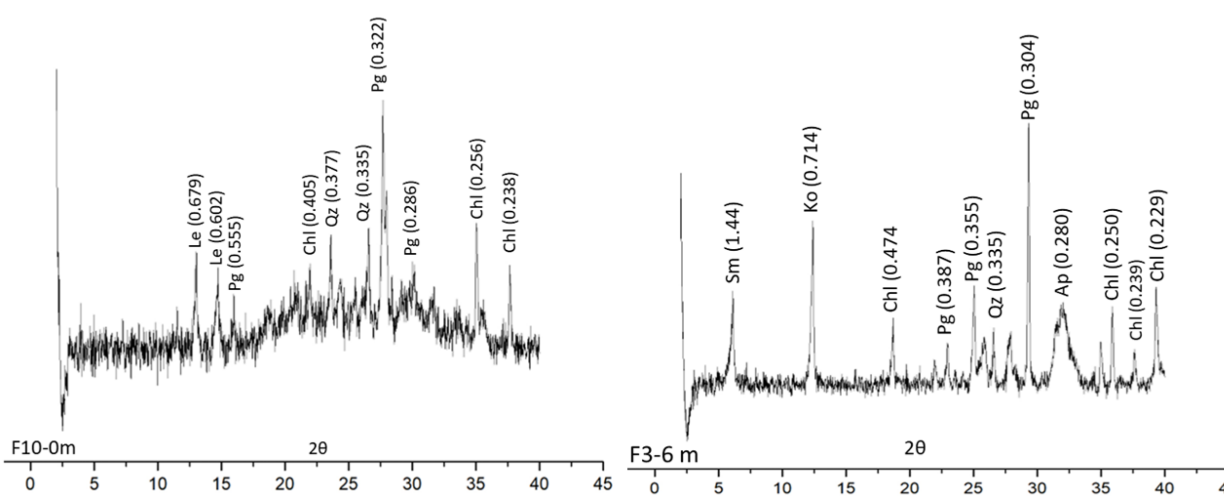

Figure 5. XRD of samples in F10 - 0 meters and F3 - 6 meters, respectively of cryoplanated platform and coastal domains evidencing the presence of leucophosphite and apatite composing the different phosphate assemblies. Ap: apatite, Chl: chlorite, Qz: quartz, Le: Leucophosphite, Sm: smectite, Pg: plagioclase.

feldspars (Boyer 1975, Bockheim 1980, Gibson et al. 1983, Campbell & Claridge 1987, Borchardt 1989, Vennum & Nejedly 1990, Hillenbrand & Ehrmann 2001).

Leucophosphite was identified mainly in nests on the CP, suggesting guano mineralization under recent nest conditions (Pereira et al. 2013, Rodrigues et al. 2021a). Vivianite was identified in nests under volcanic stacks (andesitic basalt) in the MT. These phosphate minerals seem to have originated by apatite dissolution in substrates with Fe and K (forming, leucophosphite and vivianite, respectively). According to Blume et al. (1997) vivianite can only be formed in well-drained, acidic environments with reduction conditions. The presence of this phosphate assembly suggests an intermediate to advanced phosphatization degree (Tatur 1989, Tatur & Keck 1990), corresponding to what is observed in active or recently abandoned penguin activities. These results are compared with those of Tatur & Myrcha (1989), wich also observed in the soils of areas colonized by *M. gigantau* nests, abundance of phosphate minerals linked to Al and Fe.

Several secondary silicate and phosphatic minerals were identified, indicating that, as in penguin-nesting areas, G. petrels and B. skuas may also contribute to mineralogical evolution in ornithogenic soils.

Major and trace elements

The mean of major and trace elements is show in the Table II. The averages of almost all elements are higher in MT nests, with smaller standard deviations.

The mean range of the most abundant major elements (mg/kg) were for Al (57361; 46443), Ca

Table II. Summary statistics of the elemental composition of top soils from Harmony Point.

	Marine Terrace (n= 44)					Cryoplanated Platform (n= 66)				
	Mean	**SD**	**CV %**	**Min.**	**Max.**	**Mean**	**SD**	**CV %**	**Min.**	**Max.**
Al	57361	22279	38.84	11675	128458	46339	5886	12.7	34109	60534
Fe	42656	18987	44.51	8398	85812	42534	5918	13.91	30898	55778
Ca	49849	25112	50.38	22518	135245	26362	6126	23.24	13001	45185
K	3859	1774	45.97	621	9334	2690	596	22.18	1568	4670
Mg	10968	4261	38.85	4249	23547	9428	2858	30.31	2737	15203
Na	14182	5935	41.85	2904	31826	11494	1981	17.24	7395	16799
P	15521	10463	67.41	38	40698	17685	10787	60.99	1711	54412
S	2083	1107	53.15	349	5063	1591.80	393	24.69	668.20	2458.80
Ti	4415	2115	47.90	222	8168	5725	954	16.66	2365	8121
Mn	680.4	293.10	43.08	254.9	2287.10	542.70	144.7	26.66	242.10	840.80
Zr	80.95	39.66	48.99	16.55	165.86	103.72	20.45	19.71	40.29	147.38
Ba	184.3	199.7	108.32	41.3	1172.30	66.92	13.63	20.37	44.66	112.29
Cr	19.64	9.83	50.07	8.90	52.20	22.861	7.355	32.17	12.309	43.75
Cu	141.44	65.31	46.18	30.57	330.17	77.89	33.87	43.49	28.08	224.77
Li	4.978	3.419	68.68	1.246	23.441	3.03	1.239	40.89	0.805	5.54
Sc	17.03	8.42	49.44	2.01	40.50	15.357	2.514	16.37	10.076	21.35
Sr	386.8	176.50	45.61	201.8	921.10	206.01	45.45	22.06	144.84	463.23
V	124.84	62.07	49.72	16.64	369.30	136.64	23.76	17.39	93.86	192.41
Y	17.51	10.71	61.18	1.82	40.16	11.608	3.053	26.30	4.30	18.01
Zn	156.20	109	69.76	57.70	433.90	48.26	16.21	33.59	33.19	138.58

SD: standard deviation, CV: coefficient of variation.

(49849; 26432), Na (14182; 11494) for each unit, respectively. These elements are related to the lithology composition in Harmony Point, like andesites and basaltic andesites and with the minerals identified in the XRD analyzes. Total- P was also abundant in MT (range 38 – 40698) and in CP (range 1711 – 54412). The transect variation of these mainly elements is show in the Fig. 6.

Ca is the only element that presents higher levels until 8 m of distance, in the marine terrace and the content shows a decreasing mean between 0 and 20 m in MT, showing a similar distribution like P (Fig. 6), it exhibits higher variation coefficient and standard deviation, indicating that its distribution is not regular. The Ca values can be associated to the mineralogical composition of soils, mainly by the presence of Ca-feldspars, bone fragments and guano, indicating accumulation by biogenic contribution (Tatur & Keck 1990).

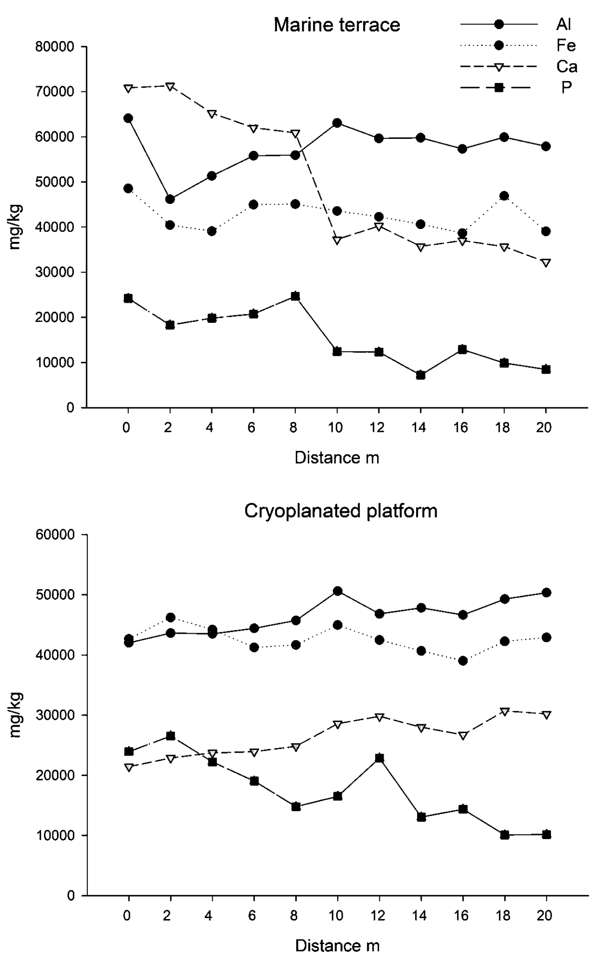

Figure 6. Variations of the mean values of the elements Al, Fe, Ca and P, along the transect (0-20 m) in the study units.

The mean of total-P distribution along the transect, showed higher concentrations at 8 m in MT (24639 mg/kg) and 12 m in the CP (22855 mg/kg) (Fig. 6).

Sodium mean concentrations are 9459 mg/kg for nests in the MT and 11529 mg/kg, in the CP. There are high levels of S in both domains, which could be explained by the hydrothermal alteration of rocks. Despite the evident sulfur enrichment insufficient which impacted the background of this element in the analyzed soils, this process was not intense enough for the formation of sulfate mineral. Samples presenting higher sulfur content were also those of more brown-yellowish color, suggesting that, even to a lesser extent, oxidation of subordinate sulfides may be contributing to weathering and soil formation. Soils developed on rocks with high contents of this element, mainly pyritized tuffs, are among the most developed of all Antarctica (Simas et al. 2006, Francelino et al. 2011, Souza et al. 2014, Lopes et al. 2019, Rodrigues et al. 2021b).

Similar concentrations was found for K, Mn and Mg, and like the other elements, present higher values in the CP than in MT. These results were also observed by Nava et al. (2008), which they attributed the higher concentrations of these elements to soils developed on volcanic plugs and the presence of calcite veins.

Cu, Sr and Zn presented higher concentrations, mainly in the MT (Table II). The Fig. 7 presents the vertical variations of these elements in the transect (0-20 m) in all collect points (F1 to F10). The three elements have a similar distribution over the transects in F6 an

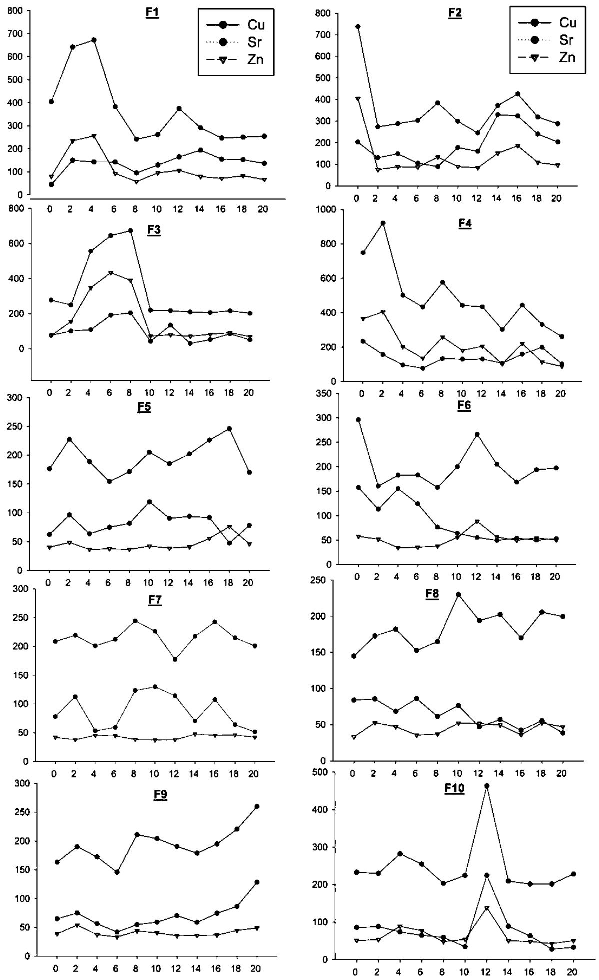

Figure 7. Vertical variations of some of the trace elements (mg/kg) in the sampling sites along the transect (0-20 m). F1 to F4 corresponding to sites in marine terrace, F5 to F10 are located in cryoplanated platform.

F10. Cu concentration is similar to mean total-P accumulations at 12 m of distance.

Cu and Zn values were higher than obtained by Pride et al. (1990) on rocks and soils of Keller Peninsula (King George Island), as well by to Navas et al. (2018) in the Elephant Point (Livingston Island). Oliveira et al. (2009) associate the gain of certain elements in soils, especially Cu and Sr, to the allochthones contribution of guano when there is no apparent source within the profile.

Tatur (1989) reported that trace element concentrations are always high in apatite-rich guano samples, generally composed of 0.52 % Sr, 0.16 % Zn and 0.09 % Cu. This may explain the significant correlation of these elements with bioavailable-P (Table SI - Supplementary Material).

Statistical of Key variables

When checking correlations between the other elements (Table SI). K positively correlates with Al, Fe, Mn and Na, the opposite to data obtained by Navas et al. (2008) in Hurd and Byer Peninsulas, where the correlation of K with Mn and Fe and Ca was negative. In the case of Harmony Point, the positive correlation points to mineralogical control.

Total-P presented negative correlation ($p < 0.05$), although weak, with Al, Na and Mn, Mg and Na; and positive correlation, although weak, with Ca, S, Cr, Cu, Sr and Zn. Whereas bioavailable-P showed significant correlation between Ca, Cu, Zn and Sr. The significant positive correlation between bioavailable-P and Ca may be indicating the preferential mineralization of P-Ca forms, as observed by Pereira et al. (2013) and Wilhelm et al. (2016).

Results of Kruskal-Wallis and ANOVA tests conducted to examine the differences of soil elemental concentrations among MT and CP (Table SII) showed that they are significantly different for almost all variables ($p \leq 0.05$), except for pH_{water} ($p = 0.838$), Sc ($p = 0.858$), and Mg ($p = 0.142$). If considered $p \leq 0.1$, both V ($p = 0.076$) and P ($p = 0.094$) showed significant differences. Results of Kruskal-Wallis tests conducted to examine the differences of soil elemental concentrations among distances (Table SIII) showed that K ($p = 0.049$) and Cation-exchange capacity at a pH of 7.0 ($p = 0.000$) are significantly different. If considered $p \leq 0.1$, P ($p = 0.094$) is also significantly different. When analyzed the differences of soil elemental concentrations among distances separated for the two soil pedogenetic units, results of Kruskal-Wallis tests showed that in MT only Cation-exchange capacity at a pH of 7.0 ($p = 0.002$) is significantly different for $p \leq 0.05$ and Ca ($p = 0.090$) for $p \leq 0.1$. On the other hand, in CP, pH ($p = 0.001$), K ($p = 0.001$), Al ($p = 0.22$), Cation-exchange capacity at a pH of 7.0 ($p = 0.002$), bioavailable-P ($p = 0.001$), Mn ($p = 0.037$), Mg ($p = 0.029$) and total-P ($p = 0.000$) are significantly different.

G. petrels and B. skuas nests: phosphatization contribution

The results showed that G. petrels and B. skuas were fundamental for soil phosphatization and consequent pedogenesis in Harmony Point. Restricted and punctual nesting of these birds, as well as population with a smaller number of individuals, not mean less intensity of phosphatization, when compared to penguins.

In general, both on the platform and on marine terraces, nesting on the tops of rocky outcrops created conditions for the formation of soils. There is a general trend of decreasing phosphorus content as it distances from the nest, with points of increasing concentrations at concordant distances. In general, the distances agree with the base of volcanic stacks (8 m) and felsenmeers (12 m), indicating the dispersion of P at the edges of elevations where nests are constructed (Fig. 8).

The accumulation of guano at the top and its dispersion up to twenty meters away from these nests, showing the importance of freezing-thawing process in the spatial distribution of phosphorus (Chen & Blume 1999). In the literature, the phosphatization promoted by these birds was restricted only inside these nestlings, due to the lower guano intake when compared to the penguin colonies (Michel et al. 2006, Pereira et al. 2013, Simas et al. 2015, Rodrigues et al. 2021c). This dispersion possibly occurs according to the morphology of the felsenmeers, so that the rich solutions of P concentrated in the fractures of the rocks and later transported by erosion.

The nests located on the CP have a more evolved pedogenic degree than on MT. As in penguin areas, upper platform usually represent areas colonized in the past, before any

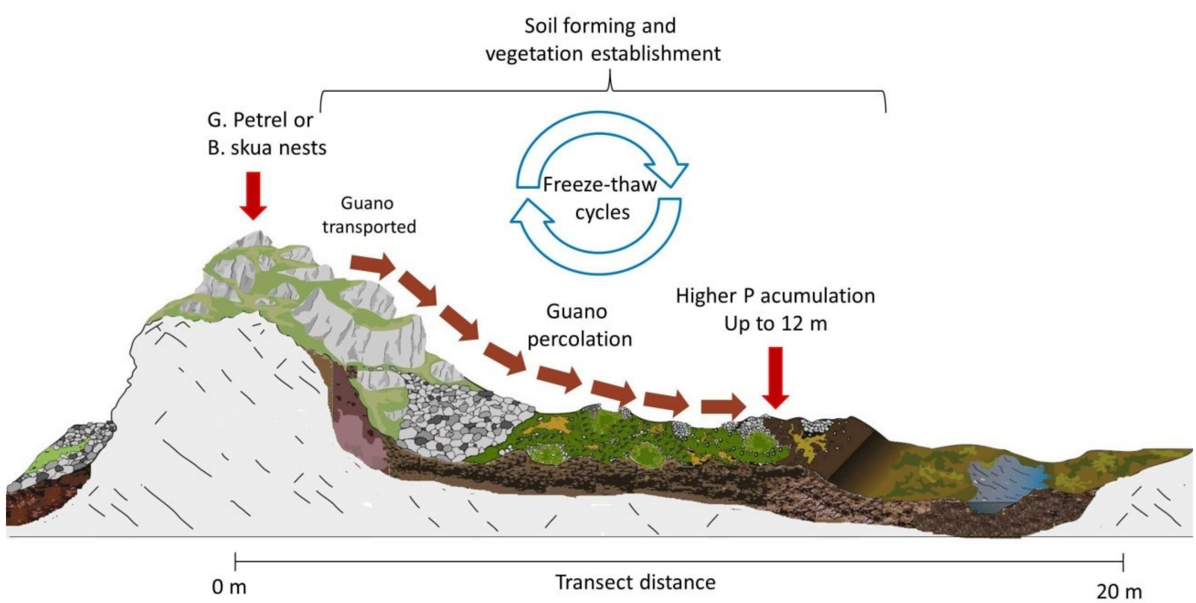

Figure 8. The diagram illustrates the organism-soil-vegetation interaction in areas of felsenmeers on the cryoplanated platform at Harmomy Point. G. petrels and B. skuas guano is the key element for the phosphating process, the dispersion on the surface is caused by the freeze-thaw cycles.

glacioeustatic uplift, and terraces are usually more recent areas (Tatur et al. 1997, Gao et al. 2018, Yang et al. 2019). These differences make the time an important factor to understand the development phosphatization degree occurs, with reflections in the mineralogy, geochemistry, chemical composition and morphology characteristics of soils. This is clearly evidenced by phosphate mineralogy, with greater presence of more stable forms of P-Fe, higher total P content, more clay soils, evidence of greater weathering of primary minerals, and greater homogeneity of chemical attributes.

In MT, the nests have more acidic substrates, more enriched in biogenic minerals, such as bone apatite, greater variation in chemical attributes, intense influence of saline spray and soils mainly composed of mineral P-Ca forms. Such coastal zone stacks have had their exposure for less than the platform. In this sense, showing recent occupation of these birds in these places, while an older nesting on the platform, favors a greater performance of the pedogenic processes.

These finds are very important to understand the development of soils in Harmony Point, and to establish two relationships: (i) development of ornithogenic soils close to the analyzed nests, classified as Ornithogenic Hemistels and Ornithogenic Sapristel by Rodrigues et al. (2019) , according to the authors, these soils have higher levels of clay, considerable amount of total carbon (average 14%) and bioavailable-P; (ii) establishment of vegetation, mainly *Sanionia uncinata* associated to *Andreaea* spp. (Rodrigues et al. 2019). Such observation is also reported by the authors Zwolicki et al. (2015), which the enrichment of nutrients derived from birds for the development of vegetation and their zones were observed at the beginning of the borders of the colonies.

CONCLUSION

This work constitutes the one of the first systematic of the phosphatization process in nests exclusively occupied by G. petrels and B. skuas. The enrichment of elements is compatible with phosphatization promoted by penguins, proving that these birds have also relevant contribution in the process of ornithogenesis in Harmony Point.

Total and bioavailable P contents are high and are distributed as follows: greater concentration at the point where the nest is located, dispersion through P-enriched solutions in fractures and erosion of the phosphatized material, creating zones of P concentration at the base of rocky outcrops colonized by birds. This process occurs mainly through freeze-thaw cycles.

Considering the presence of G. petrels and B. skuas nests in marine terrace and cryoplanated platform, several attributes were evaluated to verify distinctions between them. No significant differences were observed in total-P concentrations. However, bioavailable-P presented higher concentrations in the marine terrace, and greater variation of chemical attributes was also observed in this domain. The phosphatization in the cryoplanated platform seems to be more developed, which may be related to the time of permanence of nests in these landscape positions.

In this study, the results shows the relationships between parent material-soil-vegetation-organisms, around the felsenmeers, demonstrating these soil formations environment can be considered a hotspot inside the cryoplanated platform. This relationship demonstrates a temporo-spatial interaction, it reaches an average distance of 20 m in each evaluated nest, as shown in this study, most evolved on the cryoplanated platform and initial on the marine terraces. It shows great influence of these birds not only in soil formation, but also in plant colonization in Harmony Point.

Acknowledgments

The authors acknowledge CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) and FAPEMIG (Fundação de Amparo à Pesquisa do Estado de Minas Gerais) for financial support. We are grateful to INCT da Criosfera, TERRANTAR and MARINHA DO BRASIL (PROANTAR PROGRAM) for financial support and field assistance.

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SUPPLEMENTARY MATERIAL

Tables SI, SII, SIII.

How to cite
RODRIGUES WF, DE OLIVEIRA FS, SCHAEFER CEGR, LEITE MGP & TORRES IC. 2024. Contribution by Giant petrels and Brown skuas to soil phosphatization in Harmony Point - Maritime Antarctica. An Acad Bras Cienc 96: e20230529. DOI 10.1590/0001-3765202420230529.

Manuscript received on May 12, 2023;
accepted for publication on November 23, 2023

WILLIAM F. RODRIGUES[1]
https://orcid.org/0000-0003-0980-282X

FÁBIO S. DE OLIVEIRA[2]
https://orcid.org/0000-0002-1180-6363

CARLOS ERNESTO G.R. SCHAEFFER[3]
https://orcid.org/0000-0001-7060-1598

MARIÂNGELA G.P. LEITE[1]
https://orcid.org/0000-0002-9789-3786

ISABELA C. TORRES[3]
https://orcid.org/0000-0001-7500-7870

[1]Universidade Federal de Ouro Preto, Departamento de Geologia, Rua Pandiá Calógeras, s/n, 35400-000 Ouro Preto, MG, Brazil

[2]Universidade Federal de Minas Gerais, Instituto de Geociências, Departamento de Geografia, Av. Antônio Carlos, 662, 31270-901 Belo Horizonte, MG, Brazil

[3]Universidade Federal de Viçosa, Departamento de Solos, Av. P.H. Rolfs, 36570-000 Viçosa, MG, Brazil

Correspondence to: **William Fortes Rodrigues**
E-mail: willfordrigues@gmail.com

Author contributions

Conceptualization: WFR, FSO, CEGRS; Methodology, Writing - original draft preparation: WFR, FSO, CEGRS, MGPL and ICT; Formal analysis and investigation: WFR, FSO; Writing - review and editing: FSO, CEGRS, MGPL; Funding acquisition, Resources: CEGRS and MGPL; Supervision: FSO and CEGRS.