

THIAGO TORRES COSTA PEREIRA

SOLOS DE HOPE BAY, PENÍNSULA ANTÁRTICA

Tese apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Solos e Nutrição de Plantas, para obtenção do título de *Doctor Scientiae*.

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*À Deus,
À Cecília, Desirée, minha mãe, minha querida avó (in memoriam),
À Helena, minha querida filha,
Dedico.*

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BIOGRAFIA

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RESUMO

PEREIRA, Thiago Torres Costa, D.Sc., Universidade Federal de Viçosa, junho de 2012. **Solos de Hope Bay, Península Antártica**. Orientador: João Carlos Ker. Coorientadores: Carlos Ernesto Gonçalves Reynaud Schaefer e Raphael Bragança Alves Fernandes.

A Antártica representa um ambiente peculiar para formação de solos e estudo de muitos de seus processos. Os solos são formados em áreas livres de gelo costeiras e vales glaciais entre cadeias de montanhas, representando 0,32 %, ou 45.000 km² do continente. A respeito do aumento das pesquisas nos últimos anos, poucos estudos em solos e permafrost na Antártica focaram a área peninsular, onde transições climáticas ocorrem entre as Ilhas Shetlands do Sul, úmidas, e o Mar de Weddell, seco. Os estudos deste trabalho se concentraram em Hope Bay, situado no extremo norte da Península Antártica, representando a transição entre estas duas áreas. Atualmente, é inegável a influência do permafrost sobre os recursos hídricos, propriedades do solo, e desenvolvimento da vegetação. Além destes, uma série de questões estão relacionadas às mudanças no balanço de carbono em reflexo à degradação do permafrost pelo aumento de temperatura. Estas regiões com presença de permafrost são fortemente sujeitas a elevadas transferências de energia em superfície, cujos ecossistemas são reconhecidamente sensíveis às mudanças climáticas, sendo o estudo e monitoramento do permafrost e camada ativa, muito significativos em pesquisas prognósticas envolvendo tais mudanças. Além das questões envolvendo o regime térmico, outras relacionadas com o aporte de materiais orgânicos depositados principalmente por pinguins, que resultam na formação dos minerais de argila fosfatados e na caracterização dos solos ornitogênicos, são fundamentais para o entendimento dos processos de pedogênese local e relações ecológicas das regiões costeiras. Como suporte aos estudos, características morfológicas, físicas, químicas e mineralógicas foram trabalhadas de modo a avançar no entendimento não somente sobre os solos em Hope Bay, mas também, compreendendo o reflexo da transição climática sobre as diferenciações pedogenéticas existentes no local foco de estudo e o arquipélago das Shetlands do Sul. Além destes estudos, foram realizadas investigações micromorfológicas na tentativa de contribuir para o aperfeiçoamento dos trabalhos sobre a gênese de solos

criogênicos submetidos a condições severas de temperatura e baixa umidade. Espera-se com isso, que todos os dados e informações apontadas possam dar suporte aos estudos futuros que envolvam solos e dinâmica do permafrost em ambientes costeiros, especialmente da Península Antártica.

ABSTRACT

PEREIRA, Thiago Torres Costa, D.Sc., Universidade Federal de Viçosa, June, 2012. **Soils at Hope Bay, Antarctic Peninsula.** Adviser: João Carlos Ker. Co-advisers: Carlos Ernesto Gonçalves Reynaud Schaefer and Raphael Bragança Alves Fernandes.

Antarctica is a unique environment for soil formation and study of its processes. The soils are formed in ice-free coastal areas and glacial valleys between mountain ranges, representing 0.32%, or 45,000 km² of the continent. Regarding the increase of research in recent years, few studies in soils and permafrost at Antarctic Peninsula focused on area where climate transitions occur, between South Shetlands archipelago, humid, and the Weddell Sea, more dry. Thus, studies in this work focused on Hope Bay, located on the northern far of Antarctic Peninsula, representing the transition climate between these two areas. Currently, there is an undeniable influence of permafrost on water resources, soil properties and vegetation growth. Furthermore, other researches are related to the carbon balance due to permafrost degradation by increase of temperature. These regions that permafrost occurs are strongly subject to high surface energy transfer, whose ecosystems are notoriously sensitive to climate change, and the study and monitoring of permafrost and active layer to be significant prognostic research involving these changes. Others works related to the input of organic matter mainly by penguins, resulting in phosphatic clay minerals and ornithogenic soil formation, are fundamental to understanding the processes of pedogenesis and ecological relationships in coastal areas. Morphological, physical, chemical, mineralogical and micromorphological characteristics were studied to better understanding of soil formation at Hope Bay. The aimed was to understand the climatic transition significance on pedogenetic zonation existing between Hope Bay and South Shetlands archipelago. It is expected that all data and information studied can support future research involving soils and permafrost dynamics in coastal environments, especially at Antarctic Peninsula.

INTRODUÇÃO GERAL

O trabalho de estudo de solos de Hope Bay, Península Antártica, representa uma importante investida do Projeto Terrantar, vinculado ao Instituto Nacional de Ciência e Tecnologia da Criosfera, já que este é o primeiro estudo efetivamente realizado no continente antártico pelo referido Projeto. Até então, todos os trabalhos se concentraram no arquipélago das Shetlands do Sul. Além disso, antes do início do estudo em Hope Bay, apenas uma investigação pouco detalhada e bastante pontual havia sido realizada nos solos locais. Desta forma, destaca-se neste trabalho a apresentação dos primeiros resultados de solos de Hope Bay, alguns dos quais diferentes do que havia sido observado para solos do arquipélago das Shetlands do Sul. Assim, uma ampla comparação entre as referidas áreas foi realizada, o que permitiu observar melhor os efeitos, principalmente climáticos, sobre os solos de Hope Bay, já que a área, mais ao sul do que as ilhas Shetlands do Sul, e também mais fria e seca, representa a transição para o chamado “deserto polar” antártico.

O trabalho foi estruturado em cinco capítulos, cada um com objetivos e propostas específicas, mas que culminaram em dois objetivos principais que foram: apresentar e discutir os aspectos físicos, químicos, mineralógicos, e micromorfológicos dos solos de Hope Bay; e avaliar os dados de temperatura e umidade do permafrost e camada ativa em dois sítios de monitoramento locais.

O capítulo 1 é introdutório e se constitui em uma revisão de literatura dos assuntos tratados nos capítulos seguintes, contemplando também aspectos referentes ao uso da pedologia nos solos da Antártica realizados pelo Projeto Terrantar, bem como a ampliação da sua área de estudos.

O capítulo 2 se refere ao monitoramento de temperatura e umidade do permafrost e camada ativa de dois sítios, um sobre pinguineira ativa, e outro, distante 20 m, sobre área que já foi colonizada por pinguins, mas que atualmente, representa uma área de pinguineira abandonada. Este trabalho realizado em Hope Bay compõe uma rede maior de monitoramento elaborada pelo Projeto Terrantar e que abrange diversas áreas do arquipélago das Shetlands do Sul, além da ilha Seymour, localizada na face oriental da Península Antártica.

O capítulo 3 foi elaborado com o intuito de classificar e mostrar a distribuição

espacial dos solos em Hope Bay, além de caracterizar morfológica, física, química, e mineralogicamente os perfis representativos das classes de solos de ocorrência na área, além de tratar dos assuntos referentes à pedogênese associados às peculiaridades locais.

O capítulo 4 trata especificamente dos estudos envolvendo a pedogênese de solos ornitogênicos de Hope Bay, incluindo os aspectos ligados ao processo de fosfatização e os reflexos sobre a química e mineralogia dos solos, principalmente.

O capítulo 5 se refere ao estudo micromorfológico e microquímico dos solos ornitogênicos de Hope Bay, usados como suporte para a investigação do processo de fosfatização envolvido a partir da ocupação pelos pinguins e modificações ocorridas nos solos locais.

Com isso, a partir de capítulos cujas propostas foram abordar métodos de estudo de solos, associando permafrost e camada ativa, relacionando desde a pedogênese bem como questões envolvendo regime termal, tem-se a presente tese, elaborada como parte dos trabalhos de pesquisa do Projeto Terrantar.

CAPÍTULO 1

Pedologia brasileira na Antártica: a pesquisa de solos afetados por permafrost no cenário do aquecimento global

RESUMO

PEREIRA, Thiago Torres Costa. **Pedologia brasileira na Antártica: a pesquisa de solos afetados por permafrost no cenário do aquecimento global**. Viçosa: UFV, 2012. Cap. 1 (Tese – Doutorado em Solos e Nutrição de Plantas).

A Antártica representa um ambiente peculiar para formação de solos e estudo de muitos de seus processos, sendo que alguns dos quais possuem características atípicas. Solos afetados por permafrost são encontrados nas regiões árticas e subárticas, em altas montanhas e nas regiões livres de gelo da Antártica, e abrangem cerca de 13 % da cobertura terrestre. Atualmente, é inegável a influência do permafrost sobre os recursos hídricos, propriedades do solo, e desenvolvimento da vegetação. Além destes, uma série de questões estão relacionadas às mudanças no balanço de carbono, em reflexo à degradação do permafrost pelo aumento de temperatura. As quatro maiores regiões da criosfera no mundo são: Antártica, Oceano Ártico, as neves extra-polares e os ambientes montanhosos bastante frios. Mudanças na criosfera em resposta ao aquecimento global são prováveis de serem observadas inicialmente em zonas de transição, em torno das extremidades de geleiras e camadas de gelo, e em áreas de permafrost, ambientes que em contrapartida, influenciam, mesmo que indiretamente, todas as superfícies da Terra. O debate sobre a possibilidade da ocorrência de aumento da temperatura global causado pelos gases do efeito estufa despertou atenção de pesquisadores sobre o estado de equilíbrio das grandes massas de gelo e permafrost presentes na Antártica. Outros fatores importantes envolvem as interações que influenciam diretamente as relações tróficas e rotas de transferência de matéria e energia entre o oceano e as áreas costeiras na Antártica. Nestes locais, existe grande aporte de materiais orgânicos depositados por aves, com destaque para os pinguins, sendo a incorporação

destes materiais orgânicos à matriz mineral do solo a principal influência na caracterização dos solos ornitogênicos. Diante destes fatos, foram iniciados em 2002 os estudos pedológicos pelo então Projeto Criossolos, atual Projeto Terrantar. Os trabalhos do Terrantar, que começaram na Baía do Almirantado - Ilha Rei George, foram se expandindo ao longo das Ilhas Shetlands do Sul e Península Antártica, sendo Hope Bay, no extremo norte da Península, o primeiro trabalho efetivamente realizado no continente antártico pelo Terrantar. Diversos trabalhos foram produzidos, com destaque para as características morfológicas, físicas, químicas, mineralógicas e micromorfológicas dos solos, além de mapeamentos, em trabalhos típicos de pedologia e levantamentos de solos.

ABSTRACT

PEREIRA, Thiago Torres Costa. **Brazilian pedology in Antarctica: permafrost-affected soils in the global warming scenario**. Viçosa: UFV, 2012. Cap. 1 (Tese – Doutorado em Solos e Nutrição de Plantas).

Antarctica is a unique environment for soil formation. Permafrost-affected soils are found in Arctic and Subarctic regions, in high mountains and ice-free areas of Antarctica, and cover about 13 % of soilscape. Currently, there is an undeniable influence of permafrost on water resources, soil properties and vegetation growth, and changes in carbon balance. The four major regions of cryosphere in the world are: Antarctica, Arctic Ocean, the extra-polar snows and very cold mountain environments. Changes in cryosphere in response to global warming are likely to be observed initially in transition zones, around the ends of glaciers and ice sheets, and in areas of permafrost environments. Important factors in Antarctica involve interactions that directly influence the trophic relationships and routes transfer of matter and energy between the ocean and coastal areas. In these places, there is large amount of organic matter deposited by birds, especially penguins, and incorporation of organic materials to soil mineral matrix, that characterizes the ornithogenic process. Given these issues, were started in 2002 by Terrantar Group, studies about soils and terrestrial ecosystems. The work, that began in Admiralty Bay - King George Island, has been expanding along the South Shetland archipelago and Antarctic Peninsula. Hope Bay, on the northern far of the Peninsula, is the first studies of soils in Antarctic continent. Along the years, many works were realized, with emphasis in morphology, physic, chemical, mineralogy and micromorphology of soils, and mappings, in a typical soil surveys.

1. INTRODUÇÃO

A Antártica representa um ambiente peculiar para formação de solos e estudo de muitos de seus processos, alguns dos quais possuem características atípicas (Campbell e Claridge, 1987). A formação dos solos está intimamente relacionada à história glacial e evolução de superfícies, à geologia, e aos processos intempéricos, principalmente físicos. Incluem também nestes processos pedogenéticos a extensão e significância de fatores biológicos, como a ornitogênese/fosfatização (Tatur e Myrcha, 1989; Tatur, 2002; Schaefer et al., 2004; Michel et al., 2006; Simas et al., 2007; Schaefer et al., 2008; Simas et al., 2008), além de características como a solifluxão e crioturbação, envolvendo congelamento e descongelamento do perfil. Black (1973) considerou que estas mudanças termiais na Antártica são mais frequentes do que em qualquer outra região do mundo.

Em razão de possuir os climas mais frios e secos do planeta, a Antártica apresenta pouca água no solo, restrita a curtos períodos no verão. A água é, portanto, pouco disponível para a formação do solo, sendo o clima, muito árido em algumas regiões, capaz de dificultar ou mesmo inibir a pedogênese, os processos geomórficos, e as reações químicas (Campbell e Claridge, 1987).

A parte menos fria do continente é a Península Antártica e ilhas adjacentes, onde se concentram os trabalhos de pesquisa do Projeto Terrantar, vinculado ao Instituto Nacional de Ciência e Tecnologia da Criosfera – INCT/CNPq. Em comparação ao arquipélago das Shetlands do Sul, Hope Bay, na Península Antártica, apresenta médias de temperatura mais baixas ao longo do ano, além de menor precipitação, o que possivelmente limita a atividade pedogenética e biológica em relação às ilhas.

A ocorrência de permafrost é contínua em toda a área de Hope Bay, com setores isolados, no centro e margens da área, ricos em gelo (Scar, 2002; Martín-Serrano et al., 2005). O desenvolvimento da camada ativa e processos de *thermokarst* nestas áreas são determinados pelas condições climáticas no verão e pelo gelo superficial interconectado com água superficial e subsuperficial, sendo a evolução do permafrost nestes setores um sensível indicador de mudanças climáticas recentes e modificações do ambiente.

1.1. Projeto Terrantar: estudos pedológicos

Estudos pedológicos na Antártica realizados por brasileiros iniciaram em 2002 com o então Projeto Criosolos, atual Projeto Terrantar, vinculado ao Instituto Nacional de Ciência e Tecnologia da Criosfera – INCT, sendo que todas as atividades científicas no continente, numa esfera maior, compõem a Rede de Pesquisa do PROANTAR (CNPq/MMA/Marinha do Brasil).

Os trabalhos do Terrantar se iniciaram na Baía do Almirantado - Ilha Rei George, onde está localizada a Estação Antártica Comandante Ferraz, que teve 70 % de suas construções consumidas por um incêndio no ano de 2012.

Da Baía do Almirantado, as pesquisas de solos foram se expandindo ao longo das Ilhas Shetlands do Sul e Península Antártica, sendo Hope Bay, no extremo norte da Península, o primeiro trabalho efetivamente realizado no Continente Antártico pelo Terrantar (Fig. 1).

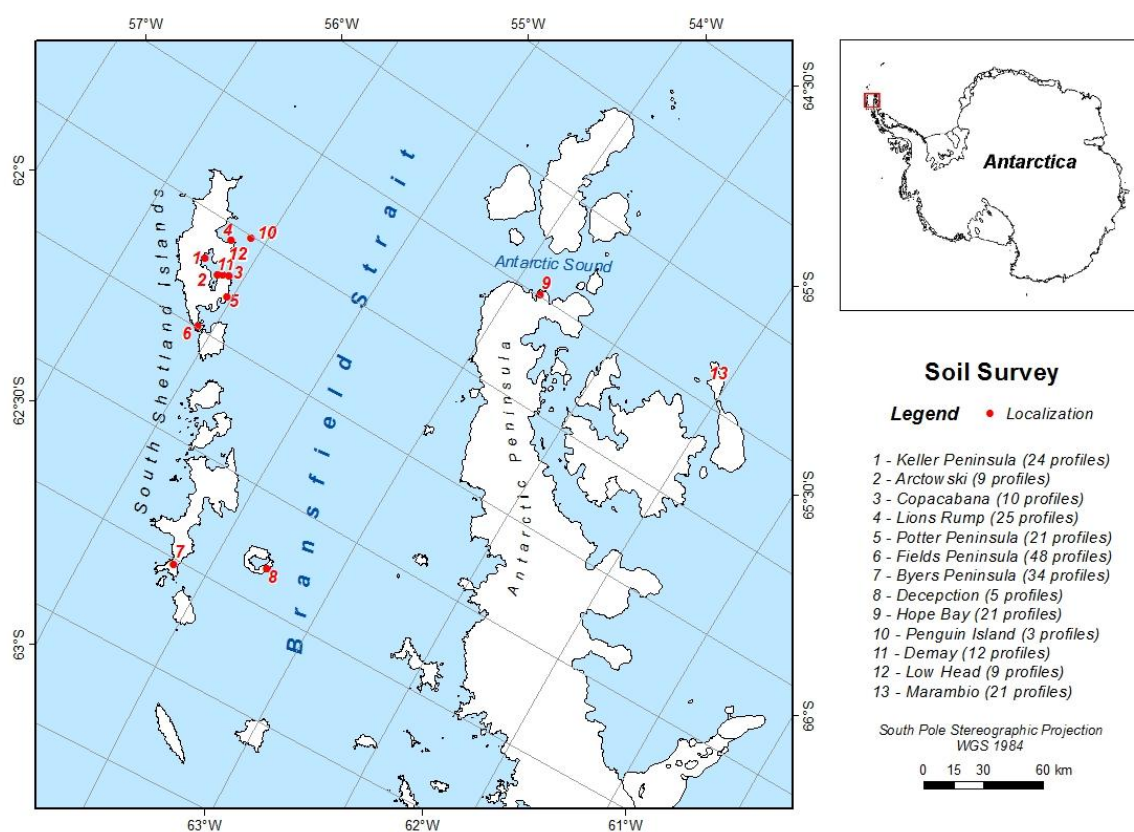


Fig. 1. Localização das pesquisas de solos realizadas pelo Projeto Terrantar na Antártica.

Mais recentemente foram realizados estudos de solos em Marambio (Ilha Seymour) e Montanhas Ellsworth, estas últimas localizadas no extremo sul da Península Antártica.

Diversos trabalhos foram produzidos envolvendo as características morfológicas, físicas, químicas, mineralógicas e micromorfológicas dos solos, além de mapeamentos, em trabalhos típicos de pedologia e levantamentos de solos. Foram produzidos também estudos específicos sobre o processo de ornitogênese / fosfatização de solos, dinâmica do carbono, indicadores bioquímicos de metais pesados e contaminantes antrópicos, química das águas de degelo, estudos de comunidades vegetais e ecologia microbiana, zonamento ambiental, geomorfologia periglacial, e monitoramento do regime térmico da camada ativa e permafrost, numa complexa rede de sensores e registradores automáticos instalados em todas as áreas estudadas.

1.2. Solos afetados por permafrost

Solos afetados por permafrost são encontrados nas regiões árticas e subárticas, em altas montanhas e nas regiões livres de gelo da Antártica. Abrangem cerca de 13 % da cobertura terrestre (Bockheim et al., 1994), e passaram, nos últimos tempos, a despertar grande interesse por serem fontes de gás, óleo e outros combustíveis fósseis (Bockheim e Tarnocai, 1998), além de serem importantes estocadores de C e água doce.

A definição de permafrost inclui toda camada de solo, sedimento ou rocha que permanece $\leq 0^{\circ}\text{C}$ por no mínimo dois anos consecutivos (ISSS Working Group RB, 2006), o que significa que a umidade para a formação de água ou gelo não necessita estar presente.

De acordo com Tarnocai (2004), solos afetados por permafrost possuem condições únicas, com propriedades físicas, químicas e biológicas diferentes daquelas encontradas em outros solos, o que estimula a compreensão sobre os processos de formação, classificação, relações ecológicas, uso e manejo, além da distribuição.

Atualmente, é inegável a influência do permafrost sobre os recursos hídricos, propriedades do solo, e desenvolvimento da vegetação em áreas periglaciais (Guglielmin et al., 2008). Além destes, uma série de questões estão relacionadas às

mudanças no balanço de carbono, especialmente devido à liberação de CH₄ e CO₂, em reflexo à degradação do permafrost pelo aumento de temperatura (Osterkamp, 2003; Michel et al, 2006; Slaymaker e Kelly, 2007). Um modelo de estimativa climática (Matear e Hirst, 1999) sugere um aumento equivalente a 4 % do total das emissões de CO₂ no século XXI em virtude do descongelamento do permafrost. No entanto, o aumento da rede de produção primária pela maior exposição do solo e temperatura pode, em um efeito reverso, estimular o sequestro de carbono e reduzir ou mesmo balancear o carbono que foi emitido. Sem contar na possibilidade de maior precipitação dos carbonatos oceânicos, amplamente apontados nas discussões sobre aquecimento global.

Pesquisas de solos afetados por permafrost começaram na Rússia, em 1906. No entanto, nas áreas livres de gelo da Antártica, ainda são incomuns os estudos e mapeamentos de solos (Goryachkin, 2004), a inferir-se pela distribuição dos solos mundiais (*World Soil Resources* - FAO, 2003; *Global Soil Regions* - NRCS, 2005), que não contemplam o continente com nenhuma classe de solo atribuída às legendas. E dentre todas as regiões da Antártica, a Antártica Marítima ainda representa uma das áreas menos conhecidas em termos de estudos de solos e permafrost (Tatur, 1989; Bockheim e Ugolini, 1990; Schaefer et al., 2004; Michel et al., 2006; Simas et al., 2008).

Na década de 1980, a Associação Internacional do Permafrost (IPA) e a União Internacional de Ciência do Solo formaram o *Cryosol Working Group*, que iniciou os esforços para melhorar a classificação dos solos com permafrost. Desses esforços surgiram as classes dos *Gelisols* (*Soil Taxonomy*) e *Cryosols* (WRB).

Nos ambientes de permafrost, cada efeito (energia e equilíbrio de massa) é manifestado ao longo da camada ativa, que é a camada de solo sobrejacente ao permafrost (Tarnocai, 2004). Para a Antártica Marítima, temperaturas não tão baixas e maior disponibilidade de água resultam em um aprofundamento desta camada, favorecendo a cobertura vegetal e o intemperismo mineral (Campbell e Claridge, 1987; Blume et al., 2004; Guglielmin et al., 2008), refletindo em solos com maiores teores de partículas finas (silte + argila), comparativamente aos solos dos desertos polares (Simas et al., 2008).

Na camada ativa, ciclos contínuos de congelamento e descongelamento favorecem a solifluxão e a formação de feições típicas, como solos com padrões (*patterned grounds*) (Bockheim e Tarnocai, 1998; Tarnocai et al., 2004). Além

destas, horizontes quebrados ou irregulares, orientação vertical de rochas dentro do perfil, movimentação e incorporação de materiais orgânicos em subsuperfície, formação de revestimentos silto-argilosos e expulsão de materiais mais finos para a superfície (*frost heave*) são comumente observados (Simas et al., 2008). Configuram-se desta forma os horizontes crioturbadados, definidos como aqueles que são irregulares ou quebrados, contendo materiais incorporados de outros horizontes, e mostrando ordenamentos verticais e horizontais (ACECSS, 1987).

A crioturbação, que é dominante em regiões de permafrost e se refere a todo movimento de solo causado por ação do congelamento/descongelamento (Bryan, 1946; Tarnocai e Zoltai, 1978; Washburn, 1980; French, 1996), inclui grandes modificações na morfologia e micromorfologia dos solos, tais como a formação de estrutura granular ovóide dos Criossolos, atribuída a congelamento/descongelamento diferencial e ultradissecção de partículas finas de solo durante processos de congelamento (Schaefer et al., 2004; van Vliet-Lanöe et al., 2004).

De modo geral, a crioturbação é favorecida, mas não restrita, a condições de drenagem imperfeita, material parental siltoso, ciclos frequentes de congelamento-descongelamento, e permafrost dentro de 1 m da superfície (Washburn, 1980; Vandenbergue, 1988). Dois modelos têm sido empregados para explicar o processo de crioturbação (Vandenbergue, 1988). O modelo “crioestático” envolve duas frentes de congelamento movendo em direções opostas, para baixo da superfície e para cima do *permafrost table*, causando pressão nos materiais descongelados presentes entre as frentes de congelamento. No modelo de “equilíbrio de células convectivas”, um processo de ascensão-subsidência no topo da camada ativa produz uma rede com movimentos de material para cima e para baixo. Este processo de ascensão-subsidência combina para produzir um tipo lento de célula de circulação cuja tendência é a ascensão (Mackay, 1980), sendo este processo um dos responsáveis pela configuração dos solos com padrões (polígonos, círculos, estrias, etc).

A crioturbação é usada em nível categórico alto nos modernos sistemas taxonômicos para diferentes solos que contenham permafrost. Sendo assim, é essencial que taxonomistas de solos sejam capazes de identificar feições de crioturbação para classificar solos afetados por permafrost (Bockheim e Tarnocai, 1998). De acordo com os autores, os processos criopedogênicos, incluindo a crioturbação, representam processos típicos e dominantes na formação de solos afetados por permafrost.

1.3. Antártica no cenário do aquecimento global

As quatro maiores regiões da criosfera no mundo são: Antártica, Oceano Ártico, as neves extra-polares e os ambientes montanhosos muito frios (Slaymaker e Kelly, 2007). Mudanças na criosfera em resposta ao aquecimento global são prováveis de serem observadas inicialmente em zonas de transição, em torno das extremidades de geleiras e camadas de gelo, e em áreas de permafrost, ambientes que em contrapartida, influenciam, mesmo que indiretamente, todas as superfícies da Terra (Tedrow, 2004; Slaymaker e Kelly, 2007).

Na Antártica, o manto de gelo que a recobre, com cerca de 14 milhões de km² e espessura que supera os 4000 m em alguns locais, correspondendo a um volume de aproximadamente 30 milhões de km³, notabiliza-se por conter aproximadamente 75 % da água doce do mundo (Campbell e Claridge, 1987; Slaymaker e Kelly, 2007). De acordo com Rocha-Campos e Santos (2001), a expressividade do gelo na Antártica faz deste continente o maior “sorvedouro” de calor da Terra, influenciando profundamente as condições climáticas, a circulação das águas oceânicas e a atmosfera terrestre.

O debate sobre a possibilidade da ocorrência de aumento da temperatura global causado pelos gases do efeito estufa despertou atenção de pesquisadores sobre o estado de equilíbrio das grandes massas de gelo e permafrost presentes na Antártica.

Estimativas indicam que o derretimento do manto de gelo austral provocaria uma elevação de até 60 m no nível do mar, com consequências catastróficas sobre a vida das populações litorâneas (Rocha-Campos e Santos, 2001). A média global do nível do mar subiu entre 0,1 e 0,25 m nos últimos 100 anos (Houghton et al., 1996). Projeções otimistas de mudanças futuras até 2100 são de acréscimo de 1 m no nível dos oceanos (National Geographic, 2007).

No inverno antártico, a área de flutuação de gelo ao redor do continente (17-20 milhões de km²) é maior que o gelo do próprio continente. Neste caso, uma esperada redução desta cobertura de mar congelado, em resposta ao aquecimento global, possivelmente provocará uma maior absorção da radiação solar (Setzer et al., 2004). Na Península Antártica, são esperadas mudanças pela maior exposição de

rochas e solos, com alterações na ecologia, especialmente com a introdução de plantas exóticas e animais (Slaymaker e Kelly, 2007).

A neve, também responsável pela regulação da temperatura na Antártica, reflete aproximadamente 80 % da radiação do sol. Em comparação, solo exposto e vegetação absorvem aproximadamente oito vezes mais radiação do que uma cobertura de neve (Slaymaker e Kelly, 2007). Neste caso, quantidades de solo cobertos por neve são criticamente importantes para o balanço de radiação terrestre e também para os sistemas climáticos globais. Além disso, neve e gelo também funcionam como isolantes, pela baixa condutividade térmica, se comparada com superfícies de solo.

Estudos em crioconitas, partículas escuras de poeira glacial inicialmente identificadas pelo explorador sueco A. E. Nordenskjöld em 1870, foram apontados mais recentemente como de grande interesse para a comunidade científica, sobretudo relacionados com sua composição e impactos nos glaciares e coberturas de neve (Schwartzman e Tedesco, 2011). Podem surgir *in situ*, a partir de quebras de rochas na superfície do gelo ou liberação de detritos presos dentro de glaciares, a partir do derretimento, ou mesmo transportadas por sistemas de circulação atmosférica global.

A crioconita destaca-se em dois aspectos: primeiro por formar sistemas biológicos isolados, de grande interesse para estudos de desenvolvimento de ecossistemas; e segundo e mais importante para o presente trabalho, relacionado ao decréscimo no albedo, maior absorção de energia e derretimento de gelo e neve. Assim, quando agregados de crioconita passam a formar buracos nos glaciares e coberturas de neve, pela redução drástica do albedo, um efeito é o aumento na ablação (Takeuchi, 2002). Fountain et al. (2004) apontam que buracos formados pela crioconita no Glaciar Canadá (*McMurdo Dry Valleys* – Antártica) contribuíram com 13 % do total do *runoff* do glaciar, apesar de cobrir apenas 4,5 % deste.

Schwartzman e Tedesco (2011), em trabalho comparativo com partículas de crioconita coletadas na Antártica e Groenlândia, apontam para um maior tamanho e maior potencial deteriorativo das partículas na Antártica, que possuem baixa reflectância influenciada principalmente pela constituição mineralógica. Tal fato é compreensível uma vez que na Antártica partículas menores tem forte ligação com a litologia em virtude do forte efeito crioclástico na redução de seus tamanhos.

1.4. Criossolos (*Gelissolos*) Ornitogênicos

A formação e duração de ecossistemas terrestres fortemente enriquecidos pelo aporte de dejetos animais têm sido relatada nos eventos geológicos. A disponibilidade restrita de áreas costeiras livres de gelo e a queda na reprodução durante a última glaciação reduziram o número de vertebrados marinhos nos solos antárticos, sendo que alguns autores consideram menor a redução das populações de pinguins, especialmente *Pygoscelis adeliae* e *Pygoscelis papua*, neste período devido à maior adaptação fisiológica destas espécies (Tatur e Myrcha, 1989; Tatur, 2002). O processo de deglaciação, com mudança na extensão dos bancos de gelo, seguida pela elevação glacio-isostática das terras durante o Holoceno, determinou o acesso dos vertebrados marinhos às terras durante os verões (Baroni e Orombelli, 1994).

Nos curtos períodos de verão, ocorrem nos ambientes terrestres, interações que influenciam diretamente as relações tróficas e rotas de transferência de matéria e energia entre o oceano e as áreas costeiras na Antártica (Rakusa-Suszczewski, 1993). Nestes locais, existe grande aporte de materiais orgânicos (guano, urina, penas, casca de ovos, restos animais/vegetais e conchas) depositados por aves e mamíferos, com destaque para os pinguins, sendo a incorporação destes materiais orgânicos à matriz mineral do solo a principal influência na caracterização dos solos ornitogênicos (Tatur e Myrcha, 1989; Tatur e Myrcha, 1993), termo que tem sido amplamente utilizado na literatura (Tedrow e Ugolini, 1966; Allen e Heal, 1970; Ugolini, 1970; Ugolini, 1972; Tedrow, 1977; Campbell e Claridge, 1987; Bockheim e Ugolini, 1990; Blume et al. 1997; Schaefer et al., 2004). De acordo com Rakusa-Suszczewski (1980), cada população de pinguim na Antártica (entre 30.000 e 50.000 casais) deposita em torno de 6,35 t de excreta no solo diariamente (comparativamente, todos os pássaros voadores depositam apenas 0,14 t), sendo que a intensidade de aporte nas pinguineiras chega a 10 kg m⁻² de excreta durante uma estação. Segundo Ugolini (1972), isto representa a mais abundante fonte de matéria orgânica nos ecossistemas terrestres antárticos.

Considerando somente a população de pinguins da Antártica Marítima, o depósito anual atinge aproximadamente 1,11 t de excreta no solo (Myrcha e Tatur, 1991). Porém, ao contrário das áreas secas do mundo, onde o guano depositado é acumulado, a maioria dos nutrientes carregados para as terras por pinguins rapidamente retornam ao mar como guano em suspensão parcialmente mineralizado. Desse montante, sob condições favoráveis, mais de 11 % do fósforo depositado pode

permanecer no solo (Myrcha et al., 1991), indicando que nesta transferência, a concentração e aumento do *turnover* podem ser importantes para a produtividade, estrutura e distribuição dos ecossistemas costeiros pobres em nutrientes.

Nas áreas extremamente frias e áridas da Antártica, a deposição do guano aparentemente tem pouca influência na alteração dos minerais (Ugolini, 1972). No entanto, sob as condições climáticas úmidas da Antártica Marítima, a intensa crioturbação e percolação de água incorporam detritos de aves em profundidade no perfil. Lixiviados ricos em P nestes sistemas reagem com o substrato mineral em um complexo processo de fosfatização do solo, primeiramente descrito por Tatur e Barczuk (1985) e recentemente estudado por Schaefer et al. (2004), Michel et al. (2006), Simas et al. (2006) e Simas et al. (2007). Assim, o fósforo, neste processo, ocorre em zonas de rochas fosfatizadas como Ca-fosfato e Fe-Al-fosfato, formados pela ação de soluções quimicamente reativas liberadas pelo intemperismo dos depósitos fosfáticos (incluindo o guano) sobre a rocha. Estas feições são muito observadas em superfícies rochosas mais susceptíveis à alteração, como basaltos e calcários, em detrimento de granitos e quartzitos (Tatur, 2002).

Nestes solos é observada a ocorrência de diversos minerais de argila fosfatados, incomuns em solos de outros ambientes naturais do planeta (Tatur e Myrcha, 1989; Tatur, 2002), apesar de terem sido encontrados também em ilhas oceânicas brasileiras a partir do aporte de materiais orgânicos depositados por aves (Oliveira et al., 2010).

Schaefer et al. (2008), por meio de microscopia eletrônica de varredura (EDS e WDS), observou feições de iluviação particulares do processo de fosfatização em ambiente criogênico, com intensa mobilidade de P e neoformação de minerais secundários fosfatados como taranakita, minyulita e leucofosfita. Uma estrutura granular, sub-arredondada composta por partículas de silte rodeadas por fosfato iluvial são típicas nos horizontes ornitogênicos (Simas et al., 2007). Em trabalho com extrações sequenciais de P em solos da Baía do Almirantado, estes autores observaram que fases moderadamente lábeis de Al-P e Fe-P são as principais frações dos sítios estudados. Estes fatos corroboram com Simas et al. (2006) que mostraram que a maior parte da fração argila em alguns solos ornitogênicos é composta por fosfatos de Fe e Al, com alta participação de formas pouco cristalinas e orgânicas.

Simas et al. (2006) observaram que fosfatos cristalinos ocorrem somente em solos diretamente afetados por pinguins (pinguineira ativa e abandonada). A

dissolução incongruente de fosfatos cristalinos de Al-Fe com formação de fases amorfas ricas em P é considerada a mais comum transformação na medida em que aumenta a idade dos sítios abandonados (Tatur et al., 1997) e mantém elevados os níveis de formas de P-lábil. Em contrapartida, nos sítios sob influência indireta dos pinguins, a entrada de P é baixa e nenhum fosfato cristalino está presente. Assim, as características químicas destes sítios são controladas por P minerais altamente reativos e não cristalinos.

Solos ornitogênicos distinguem-se claramente daqueles não ornitogênicos por várias características, como baixo pH (devido ao alto grau de nitrificação) e saturação por bases; teores muito elevados de P (Mehlich-1), Al trocável, COT e N total. O conteúdo de partículas finas (silte + argila) são usualmente mais baixos, possivelmente devido à destruição de aluminossilicatos por acidólise, que ocorre nestes solos pela decomposição microbiana do guano fresco, gerando ácido nítrico e sulfúrico (Tatur et al., 1997). Apresentam clara diferenciação entre horizontes, sendo o horizonte A relativamente profundo e rico em matéria orgânica (formando um epipedon umbrico), e horizonte B fosfático (discretamente acinzentado e amarelado) (Simas et al., 2007).

Em alguns destes solos, observa-se o desenvolvimento de oásis com extensa e contínua cobertura vegetal, nos quais se verificam maior atividade microbiológica em termos de solos antárticos (Tatur et al., 1997; Michel et al., 2006).

Nas pinguineiras ativas, a contínua deposição do guano fresco e pisoteio das aves inibe o estabelecimento da vegetação (Tatur, 1989; Tatur et al., 1997). Nos solos localizados próximos a estas pinguineiras ativas, ou em pinguineiras abandonadas, a influência ornitogênica e o reflexo na cobertura vegetal são bastante pronunciados, com possível formação de um horizonte superficial humificado, distinguido por uma coloração escura e relações C/N e C/P mais altas do que em materiais ornitogênicos (Tatur et al., 1997). Nestas áreas a colonização inicia-se com a formação de uma cobertura de *Prasiola crispa* (algae). Normalmente em posições mais altas da paisagem, antigas pinguineiras são hoje muito colonizadas por líquens, briófitas, e por duas espécies superiores: *Deschampsia antártica* (gramineae) e *Colobanthus quitensis* (cariofilaceae).

Em função de sua distribuição geográfica limitada, sítios ornitogênicos são extremamente importantes e constituem o mais importante lócus de sequestro de C nos ecossistemas terrestres antárticos (Michel et al., 2006; Simas et al., 2007), já que

embora a produção de biomassa pela vegetação antártica seja relativamente baixa, ela frequentemente excede a capacidade de decomposição da microbiota local (Ugolini, 1972).

Pouco são os conhecimentos a respeito da dinâmica do C nos solos antárticos e qual seu papel no ciclo global do C, comparativamente a solos de outros ecossistemas (Michel et al., 2006). Segundo os autores, um entendimento do ciclo do C nos solos ornitogênicos da Antártica é importante para a compreensão dos efeitos do aquecimento global nos ambientes costeiros deste continente. Ácidos húmicos extraídos de Criosolos Ornitogênicos da Antártica Marítima são ricos em N e são facilmente termo-degradados, sugerindo que estes solos sejam vulneráveis à perda de C para a atmosfera em resposta ao aquecimento global (Michel et al., 2006).

Além dos pinguins, outras espécies também contribuem para o processo de ornitogênese, no entanto de fraca intensidade, como as skuas, petréis e gaivotões (Simas et al., 2007). Observa-se desenvolvimento de vegetação em áreas mais distantes da costa próximo a ninhais destas aves, indicando a importância da fertilização dos solos por estes animais, e reflexo no estabelecimento de comunidades vegetais mais complexas e com maior capacidade de fixação de C (Michel et al., 2006).

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CAPÍTULO 2

Regime térmico da camada ativa e permafrost em solos de Hope Bay, Península Antártica: implicações ambientais

RESUMO

PEREIRA, Thiago Torres Costa. **Regime térmico da camada ativa e permafrost em solos de Hope Bay, Península Antártica: implicações ambientais**. Viçosa: UFV, 2012. Cap. 2 (Tese – Doutorado em Solos e Nutrição de Plantas).

Regiões polares e subpolares com presença de permafrost são fortemente sujeitas a elevadas transferências de energia em superfície, cujos ecossistemas são reconhecidamente sensíveis às mudanças climáticas. Desta forma, estudos e monitoramento do permafrost e camada ativa podem ser muito significativos em pesquisas prognósticas envolvendo tais mudanças, sendo a dinâmica das superfícies congeladas um geoindicador para o monitoramento e avaliação de mudanças ambientais. Na Antártica, a insuficiente rede de sondagens de monitoramento de temperatura do permafrost e camada ativa são os principais motivos que justificam um estudo mais avançado e de longo prazo a cerca do tema. Na Península Antártica, o clima tem experimentado uma tendência de aquecimento nos últimos 50 anos, cujas temperaturas aumentaram em aproximadamente 2,5 °C. Devido à região estar localizada próxima do limite latitudinal do permafrost, torna-se necessário o entendimento de como o ambiente reage a esta alteração climática, cujo cenário ainda é pouco conhecido. Assim, foi objetivo deste trabalho avaliar os resultados do monitoramento de temperatura do solo e ar e umidade do solo em dois sítios localizados em Hope Bay, um representado por pinguineira ativa (S1), e outro, ao lado, não mais ocupado pelos pinguins (S2). Para tanto, foi utilizada uma unidade *datalogger* (CR1000 - Campbell Scientific, INC), que coletou dados de temperatura e conteúdo de água no solo e temperatura do ar, a cada hora, durante os anos de 2009-2011. Foram calculados o índice *Freezing Degree Days* (FDD) e o índice *Thawing Degree Days* (TDD) e o Fator-N. A deposição de guano em S1 representa importante

fator para maiores resultados de TDD decorrentes de intensa atividades dos pinguins e reações químicas provocadas pela decomposição do guano. Em S2, localizado em uma posição mais baixa na encosta, que provavelmente favoreceu a maior espessura e ocorrência de neve por mais tempo, as maiores médias mínimas de temperatura evidenciam a capacidade de isolamento térmico da neve e a diferenciação microclimática decorrente do ambiente onde ocorrem, e que consequentemente resultou em resultados de FDD maiores do que os encontrados no S1. O provável maior acúmulo de neve em S2 refletiu nos menores resultados do Fator-N neste sítio, indicando ser este um parâmetro importante nas relações térmicas existente entre o solo e a camada de ar imediatamente acima.

ABSTRACT

PEREIRA, Thiago Torres Costa. **Thermal regime of active layer and permafrost in soils of Hope Bay, Antarctic Peninsula: environmental implications.** Viçosa: UFV, 2012. Cap. 2 (Tese – Doutorado em Solos e Nutrição de Plantas).

Regions that permafrost occurs are strongly subject to high surface energy transfer, whose ecosystems are notoriously sensitive to climate change, and the study and monitoring of permafrost and active layer to be significant prognostic research involving these changes. In Antarctic Peninsula, temperatures increased approximately 2.5 °C in the last 50 years. Due region is located near the permafrost latitudinal limit, it is necessary to understand how the environment reacts to this climate change, whose scenario is still little known. Thus, this study aimed to evaluate the results of air and soil temperature, and soil moisture at two sites in Hope Bay, represented by penguin rookery (S1), and another neighbor, not occupied by penguins (S2). Thus, it was used a datalogger (CR1000 - Campbell Scientific, Inc.), which collected data on temperature and water content in soil and air temperature, every hour, during the years 2009-2011. The Freezing Degree Days (FDD), Thawing Degree Days (TDD), and N-factor indices were calculated. The guano deposition in S1 represents an important factor for high TDD results due to intense activities of penguins and chemical reactions. In S2, located in lower position on the slope, which probably favored the occurrence of greater snow thickness, the highest mean minimum temperature show the thermal snow insulation and microclimatic differentiation where snow occur, and consequently resulted in FDD results greater than those found in the S1. The largest accumulation of snow likely in S2 resulted in lower N-factor levels, indicating this is an important parameter for thermal relationship between soil and air layer immediately above.

1. INTRODUÇÃO

Regiões polares e subpolares com presença de permafrost são fortemente sujeitas a elevadas transferências de energia em superfície (Bockheim, 1995), cujos ecossistemas são reconhecidamente sensíveis às mudanças climáticas (Guglielmin et al., 2008). Desta forma, estudos e monitoramento do permafrost e camada ativa podem ser muito significativos em pesquisas prognósticas envolvendo tais mudanças (Ramos e Vieira, 2003). Berger e Iams (1996) reforçam que a dinâmica das superfícies congeladas tem sido designada como um geoindicador para o monitoramento e avaliação de mudanças ambientais.

Na Antártica, a insuficiente rede de sondagens de monitoramento de temperatura do permafrost e camada ativa são os principais motivos que justificam um estudo mais avançado e de longo prazo a cerca do tema (Bockheim, 1995). Nesse sentido, foram implementados dois projetos do Ano Polar Internacional: *Thermal State of Permafrost – International Network of Permafrost Observations* (TSP), cujo objetivo foi caracterizar o estado térmico do permafrost em nível Global, incluindo a realização de perfurações na Antártica; e *Antarctic and Sub-Antarctic Permafrost, Soils and Periglacial Environments* (ANTPAS), cujo objetivo vincula-se à instalação de sítios de monitoramento da camada ativa conforme o protocolo *Circumpolar Active Layer Monitoring* (CALM) (Bockheim, 2005).

O projeto CALM foi estabelecido no início da década de 1990 com o objetivo de estabelecer observações de longo prazo da variação espacial e temporal da camada ativa e permafrost próximo da superfície, bem como avaliar a sua resposta às alterações climáticas (Brown et al., 2000, Nelson et al., 2008). Trata-se de um dos mais antigos e sistemáticos programas orientados para o monitoramento das mudanças climáticas do planeta (Nieuwendam, 2009).

Na Península Antártica, o clima tem experimentado uma tendência de aquecimento nos últimos 50 anos, cujas temperaturas aumentaram em aproximadamente 2,5 °C (Nieuwendam, 2009). Segundo o autor, pelo fato da região estar localizada próxima do limite latitudinal do permafrost, torna-se necessário o entendimento de como o ambiente reage a esta alteração climática, cujo cenário ainda é pouco conhecido.

No arquipélago das Shetlands do Sul e norte da Península Antártica, regiões nas quais o clima condiciona médias anuais de temperatura do ar próximas a 0 °C, o aumento da temperatura do ar e precipitação podem causar a degradação ou até mesmo o desaparecimento do permafrost em locais em que este ocorre espaçadamente (Ramos et al., 2008). De acordo com os autores, além destes, fatores responsáveis pelos fluxos de calor na camada ativa tais como a espessura e estabilidade das coberturas de neve, o teor de umidade do solo, e presença de setores com baixa condutividade térmica no perfil contribuem diretamente para o controle da espessura da camada ativa e estabilidade do permafrost. Dessa forma, o regime térmico do solo é controlado pelas trocas de calor e umidade entre a atmosfera e a superfície do solo, bem como pelas suas propriedades termofísicas.

Especificamente para Hope Bay, área situada no norte da Península Antártica, Yermolin e Silva Busso (2007) apontam que a evolução do permafrost em setores isolados de permafrost ricos em gelo é um sensível indicador recente de mudanças climáticas e modificação do ambiente. Assim, terrenos com permafrost são considerados como altamente sensíveis a distúrbios termais (Bockheim, 1995; Ramos e Vieira, 2003; Ramos et al., 2007; Slaymaker e Kelly, 2007), sendo objeto de estudo e monitoramento por diversos autores (Romanovsky e Osterkamp, 2000; Vieira et al., 2000; Ramos e Vieira, 2003; Ramos et al., 2007; Guglielmin et al., 2008; Rachlewicz e Szczuciński, 2008; Ramos et al., 2008; Nieuwendam, 2009).

Conforme Vieira et al. (2000), a utilização de registradores automáticos (*datalogger*) de temperatura e umidade do ar e do solo em várias profundidades permite obter informações sobre fluxos de frio e calor no perfil, com posterior estudo de suas reações (crioclastia, termoclastia, crioexpulsão, etc.). Além disso, o sistema tem as vantagens do monitoramento a intervalos temporais curtos e do baixo custo. No entanto, além do monitoramento e estudo, é importante o trabalho de mapeamento destas áreas, capazes não somente de mostrar a distribuição espacial de solos e permafrost, mas também de auxiliar no planejamento territorial. Nesse sentido, a interpretação dos mapas de ocorrência de permafrost funciona como guia para as áreas mais susceptíveis às mudanças ambientais, já que ambos, aquecimento e profundidade do permafrost são usados para predizer o nível de alerta (Slaymaker e Kelly, 2007).

Tais parâmetros representam o foco principal da *Global Terrestrial Network for Permafrost* (GTN-P), criada em 1998 pela *International Permafrost Association*

(IPA). Suas metas visam organizar e gerir uma rede global de permafrost com medidas de temperatura que auxiliem na detecção, monitoramento e predição de mudanças climáticas. A GTN-P contribui para o *World Meteorological Organization's Global Climate Observing System* (WMO-GCOS) e para o *Global Terrestrial Observing System* (GTOS). As sondagens com dados estão localizadas principalmente na Rússia, Canadá e Alasca, sendo a maioria das perfurações entre 10 e 125 m de profundidade (Nieuwendam, 2009).

Entre os parâmetros geocriológicos mais importantes relacionados a uma área afetada pelo desenvolvimento do permafrost causado pelo aumento da temperatura incluem o aumento da espessura do descongelamento estacional. Em Hope Bay, isto está associado tanto às mudanças do regime das águas subterrâneas, quanto ao desenvolvimento de processos de *thermokarst* e *thermoerosion* nas áreas de permafrost ricos em gelo (Yermolin e Silva Busso, 2007).

As condições climáticas, geológicas e geomorfológicas determinam a existência e estrutura do permafrost (Yermolin e Silva Busso, 2007), sendo a sensibilidade do ambiente e o processo de termoerosão de zonas com permafrost ricos em gelo subterrâneo relacionados a três causas: mudança climática associada com aumento de temperatura e espessura de descongelamento estacional; circulação de água suprapermafrost ou superficial; e resultado de alteração da superfície natural.

Assim, o objetivo deste trabalho foi avaliar os resultados do monitoramento de temperatura do solo e ar e umidade do solo de dois sítios localizados em Hope Bay, um representado por pinguineira ativa, e outro, ao lado, não mais ocupado pelos pinguins.

2. MATERIAL E MÉTODOS

2.1. Área de estudo

O trabalho foi realizado em Hope Bay, extremo norte da Península Antártica (Fig. 1). A área é delimitada ao sul pelo Monte Flora (520 m de altitude) e Circo Glacial Flora, e a leste, pelo Glaciar Buenos Aires, cuja parte cônica atinge mais de 100 m de altitude.

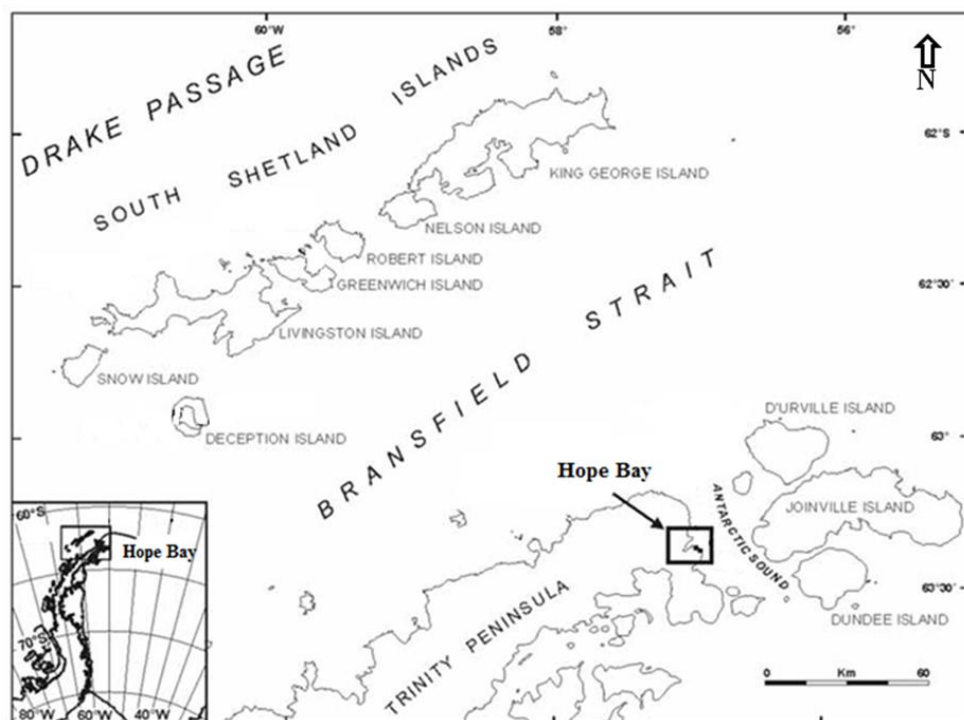


Fig. 1. Localização de Hope Bay, Península Antártica. Adaptado de Scar (2002).

De acordo com Scar (2002), a área do Monte Flora e adjacências é considerada *Antarctic Specially Protected Area* (ASPA 148). Excluindo o Monte Flora, a área livre de gelo entre o mar e os glaciares corresponde a uma região de aproximadamente 3 km², com elevações médias inferiores a 100 m (Birkenmajer, 1993a; Martín-Serrano et al., 2005).

Pela classificação de Köppen, a região enquadra-se no clima EF (polar). A temperatura média de Hope Bay fornecida pela Esperanza Station, no período entre 1952 e 2010, foi de - 5,1 °C (Fig. 2), sendo a precipitação, de aproximadamente 150 mm.

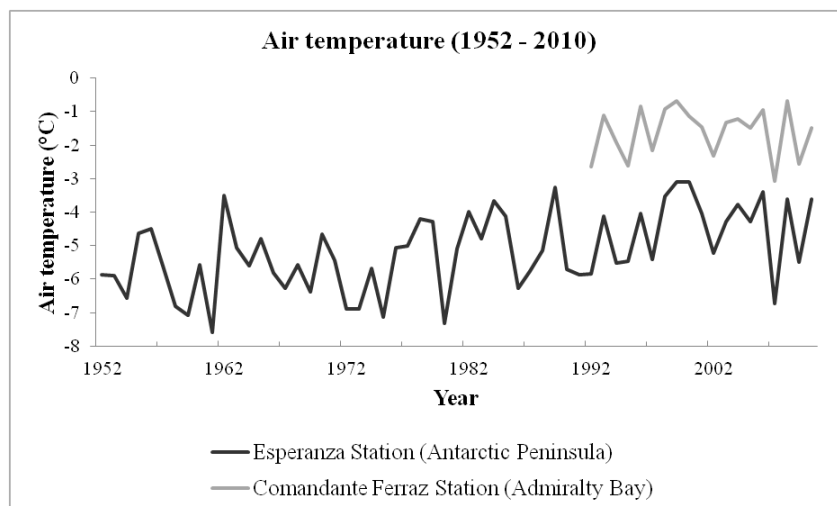


Fig. 2. Diferenças de temperatura entre Hope Bay (*Antarctic Peninsula*) e Península Keller (*Admiralty Bay – King George Island*). Fonte: Instituto Antártico Argentino e Programa Antártico Brasileiro.

A composição geológica de Hope Bay inclui rochas metassedimentares (Grupo Península Trinity - Formação Hope Bay: turbiditos siliciclásticos marinhos e arenitos), sedimentares (Grupo Botany Bay - Formação Monte Flora: arenitos, conglomerados e xistos), e vulcânicas (Grupo Vulcânico Península Antártica - Formação Glaciar Kenney: riolito-dacitos, ignimbritos, conglomerados e tufo cimentados) (Birkenmajer, 1993b; del Valle et al., 2001; Scar, 2002).

A geomorfologia está fundamentalmente relacionada a formas e processos glaciais e periglaciais, refletindo a retirada generalizada dos glaciares destas superfícies Quaternárias (Martín-Serrano et al., 2005). Subordinados a isto, existem processos ligados ao ambiente litoral, ventos, fluxos de verão, lagos e lagunas.

2.2. Monitoramento da camada ativa e permafrost

O monitoramento do permafrost e camada ativa foi realizado a partir de unidade *datalogger* instalada (CR1000 - *Campbell Scientific*, INC), que coletou dados de temperatura (sensor 105E) e conteúdo de água no solo (sensor CS616) em dois sítios selecionados e temperatura do ar (sensor 107, posicionado a 1,5 metros acima da superfície), a cada hora, durante os anos de 2009-2011.

Os sítios foram separados da seguinte forma: Sítio 1 – S1 (pingueira ativa) e Sítio 2 – S2 (borda da pingueira ativa). S2 encontra-se distante 20 m de S1, e em

posição mais baixa na encosta, com declividade inferior a 3° de inclinação. O sensor de temperatura do ar foi instalado entre os sítios de monitoramento, cujo resultado serve de referência para ambos os sítios.

As profundidades dos perfis foram determinadas seguindo critérios de incidência do permafrost, contato lítico restritivo ou profundidade máxima de 1 metro. Para a temperatura do solo, foram instalados sensores nas profundidades de 10, 30 (sensores 105E), e 80 cm (sensores 105E e CS616). Devido às condições climáticas severas, o sistema foi acondicionado em duas caixas de marfinito (uma para o aparelho e outra para a bateria – 90 A), visando melhor isolamento térmico e facilidade de manutenção.

2.3. Processamento dos dados e modelagem ambiental

Os dados de temperatura e umidade, juntamente com informações físicas e químicas dos sítios de monitoramento (dois perfis de solo) foram utilizados para estimar os parâmetros termais diários e mensais destes (Hinkel et al., 2001; Ramos e Vieira, 2003; Vieira et al., 2003; Guglielmin et al., 2008). As informações foram processadas de forma a identificar os diferentes períodos de alteração da temperatura e umidade do solo e suas consequências na dinâmica do permafrost.

Foram calculados o índice *Freezing Degree Days* (FDD), que representa o resultado da soma acumulativa das temperaturas médias diárias do solo inferiores a 0 °C (Humlum, 1998), e o índice *Thawing Degree Days* (TDD), que representa a soma acumulativa das temperaturas médias diárias do solo superiores a 0 °C (Christiansen e Humlum, 2008). Para o FDD e TDD foi considerada a profundidade de 10 cm, por ser a mais próxima da superfície do solo, e temperatura do ar. A partir dos resultados de *Freezing Degree Days* do solo a 10 cm (FDDs) e do ar (FDDa), foi calculado o índice Fator-N (FN), neste caso, apenas para o período de congelamento: $FN = FDDs / FDDa$.

3. RESULTADOS E DISCUSSÃO

Os resultados de temperatura do ar indicam médias mais baixas em 2009, quando atingiram $-7,6\text{ }^{\circ}\text{C}$. A temperatura mais baixa ocorreu no mês de julho de 2009, quando foi registrado $-30,6\text{ }^{\circ}\text{C}$, e a temperatura mais alta, em novembro de 2010, com registro de $11,8\text{ }^{\circ}\text{C}$ (Tabela 1).

Tabela 1. Temperatura do solo e ar e conteúdo de água em dois sítios de monitoramento, para um período de dois anos (2009-2011)

Sítio	TS - 10 cm	TS - 30 cm	TS - 80 cm	CA - 80 cm	TA - 1,5 m*
Média - 1	-4,95	-4,82	-4,67	0,07	-5,60
Média - 2	-4,78	-4,81	-4,73	0,05	
Mínimo - 1	-26,30	-20,30	-15,90	0,02	-30,60
Mínimo - 2	-21,70	-17,90	-15,20	0,02	
Máximo - 1	14,10	4,60	1,50	0,40	11,80
Máximo - 2	8,22	1,98	0,72	0,17	

TS: temperatura do solo em $^{\circ}\text{C}$; CA: conteúdo de água, em %; TA: temperatura do ar, em $^{\circ}\text{C}$; *metros acima da superfície do solo.

No Sítio 1 (S1), em pinguineira ativa, as temperaturas máximas e conteúdo de água disponível foram praticamente o dobro daquelas encontradas no Sítio 2 (S2), situado na borda da pinguineira ativa (Fig. 3 e Fig. 4), mostrando que as reações no solo provocadas pela deposição de guano criam verdadeiros micro-sítios ao longo da paisagem.

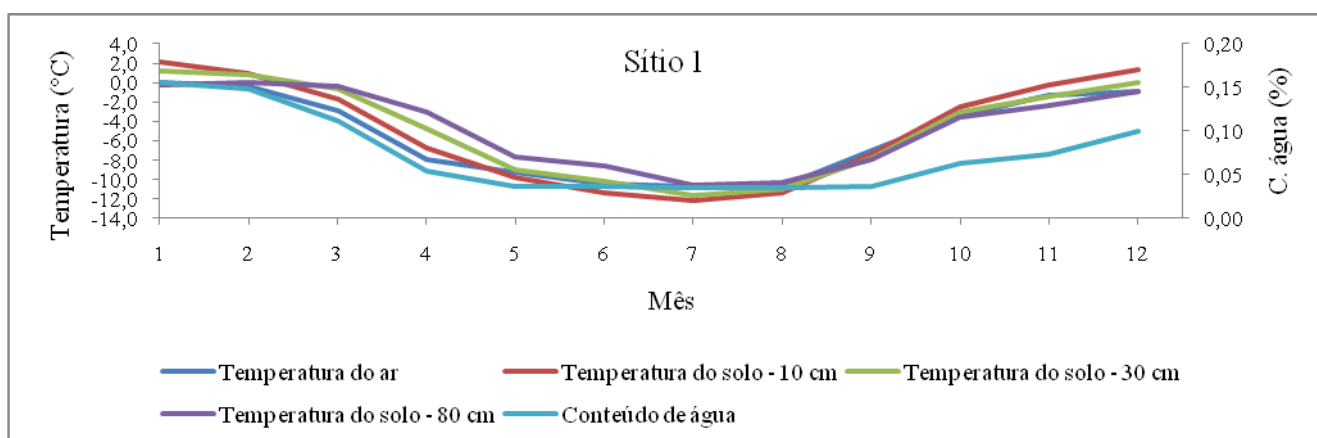


Fig. 3. Média de temperatura do solo e do ar e conteúdo de água do Sítio 1 entre o período 2009-2011 (média dos meses).

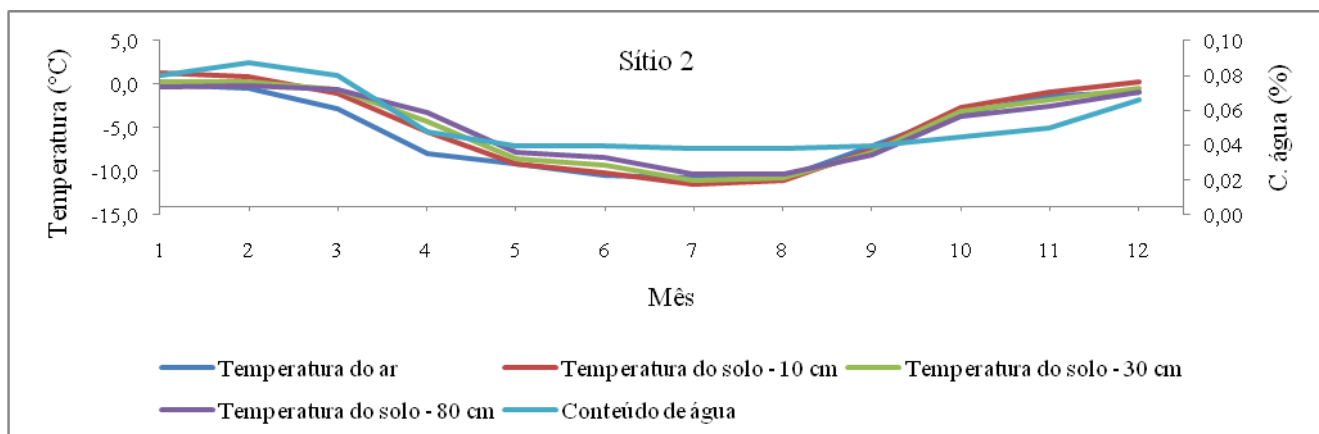


Fig. 4. Média temperatura do solo e do ar e conteúdo de água do Sítio 2 entre o período 2009-2011 (média dos meses).

Temperaturas mínimas foram, no entanto, inferiores em S1, cujos resultados aproximaram-se aos do S2 somente em 80 cm de profundidade. O fato do S1 possuir temperaturas mínimas mais significativas deve-se provavelmente à menor espessura da cobertura de neves nesse sítio, o que favorece mais as trocas de calor entre o solo e a atmosfera. O fato de S2 estar numa posição levemente mais baixa na paisagem, mesmo que distante apenas 20 m de S1, pode ter favorecido o maior acúmulo de neve. A neve nessa situação provoca um isolamento do solo, diminuindo as trocas de calor com a atmosfera, tamponando as temperaturas próximas da superfície do solo em aproximadamente 0 °C por mais tempo. Assim, tem-se a seguinte situação: S1 com temperaturas mais altas que S2 no verão, devido à intensa atividade de pinguins e deposição de guano; e S1 com temperaturas mais baixas no inverno devido à menor espessura de neve que em S2.

O índice *Freezing Degree Days* (FDD) é tradicionalmente utilizado para definir a severidade das condições climáticas e para analisar as taxas de congelamento do solo (Guglielmin et al., 2008). No entanto, mesmo abaixo de 0°C o solo nem sempre está necessariamente congelado já que o congelamento depende da combinação de temperatura e outros fatores como umidade, por exemplo.

De modo geral, a soma dos resultados mensais do FDD foram de -4021,9 °C e -3715,2 °C para S1 e S2, respectivamente (Tabela 2).

Tabela 2. *Freezing degree-days* (FDD) e *Thawing degree-days* (TDD) dos sítios monitorados

	Soma*	FDD**	Soma*	TDD**	Soma*	FDD**	Soma*	TDD**
	-----Sítio 1-----				-----Sítio 2-----			
Fev-09	-4.6		2.0		-0.3		1.8	
Mar-09	-34.1	-38.7	29.6	31.7	-15.2	-15.6	21.8	23.6
Abr-09	-170.7	-209.5	0.0	31.7	-135.9	-151.5	0.0	23.6
Mai-09	-283.0	-492.5	0.0	31.7	-262.9	-414.4	0.0	23.6
Jun-09	-482.1	-974.6	0.0	31.7	-429.9	-844.2	0.0	23.6
Jul-09	-460.2	-1434.7	0.0	31.7	-436.2	-1280.4	0.0	23.6
Ago-09	-388.1	-1822.9	0.0	31.7	-376.8	-1657.2	0.0	23.6
Set-09	-248.6	-2071.4	0.0	31.7	-244.8	-1902.0	0.0	23.6
Out-09	-134.3	-2205.7	0.1	31.8	-133.8	-2035.8	0.0	23.6
Nov-09	-78.4	-2284.1	10.5	42.3	-82.1	-2117.9	0.7	24.3
Dez-09	-6.7	-2290.9	59.9	102.2	-8.6	-2126.5	26.2	50.5
Jan-10	-2.2	-2293.1	47.3	149.4	-0.3	-2126.8	28.6	79.1
Fev-10	-12.7	-2305.9	19.6	169.0	-4.8	-2131.5	12.7	91.8
Mar-10	-107.7	-2413.6	9.6	178.6	-79.5	-2211.0	5.1	96.9
Abr-10	-233.2	-2646.8	1.7	180.3	-189.5	-2400.5	0.0	96.9
Mai-10	-321.6	-2968.4	0.0	180.3	-301.3	-2701.8	0.0	96.9
Jun-10	-201.1	-3169.5	0.0	180.3	-179.9	-2881.7	0.0	96.9
Jul-10	-295.4	-3464.8	0.0	180.3	-279.0	-3160.7	0.0	96.9
Ago-10	-315.4	-3780.2	0.0	180.3	-306.2	-3466.9	0.0	96.9
Set-10	-195.6	-3975.8	0.0	180.3	-204.0	-3670.9	0.0	96.9
Out-10	-30.5	-4006.2	7.7	188.0	-32.0	-3702.9	0.8	97.7
Nov-10	-1.1	-4007.3	52.6	240.6	-0.1	-3702.9	26.1	123.8
Dez-10	-13.8	-4021.1	41.0	281.6	-12.3	-3715.2	16.2	140.0
Jan-11	-0.7	-4021.8	86.7	368.2	0.0	-3715.2	55.1	195.1
Fev-11	-0.1	-4021.9	51.3	419.5	0.0	-3715.2	38.4	233.4

*somatório das temperaturas médias diárias do solo; **soma acumulativa das temperaturas médias diárias do solo, mês-a-mês.

As diferenças entre os dois sítos estudados evidenciam as irregularidades das condições de frio no solo, conforme observado por Nieuwendam (2009) para dois sítios de monitoramento na Antártica Marítima distantes 40 m um do outro. Além disso, mostram as diferentes influências da temperatura do solo e da provável maior espessura de neve em S2, e o modo como são determinantes para as características térmicas do solo.

Os resultados de *Thawing Degree Days* (TDD) foram de 419,5 °C e 233,4 °C para S1 e S2, respectivamente (Tabela 2). O resultado positivo maior em S1 indica provavelmente a influência da maior atividade biológica relacionada à presença dos pinguins e decomposição de guano. De acordo com Nieuwendam (2009), as diferenças entre TDD e o número de dias de solo descongelado são importantes, pois

permite uma aproximação com fluxo de calor para o solo, refletindo seus ganhos energéticos.

Resultados do Fator-N (FN) foram inferiores para o S2 nos dois anos observados (Fig. 5), até o mês de setembro, aproximadamente, reforçando uma maior influência da cobertura de neve nesse sítio pelo tamponamento de temperatura próximo a 0 °C por mais tempo, devido à sua má condução de calor. Trata-se de um parâmetro útil devido à sua simplicidade e ao potencial para determinar a relação física entre as condições da superfície do solo e atmosféricas (Karunaratne e Burn, 2003).

Nos meses entre setembro e janeiro o FN nos dois sítios passa a ter valores muito próximos devido à diminuição ou mesmo ausência de cobertura de neve, o que favoreceu as trocas de calor entre o solo e a atmosfera de maneira mais homogênea nos dois sítios.

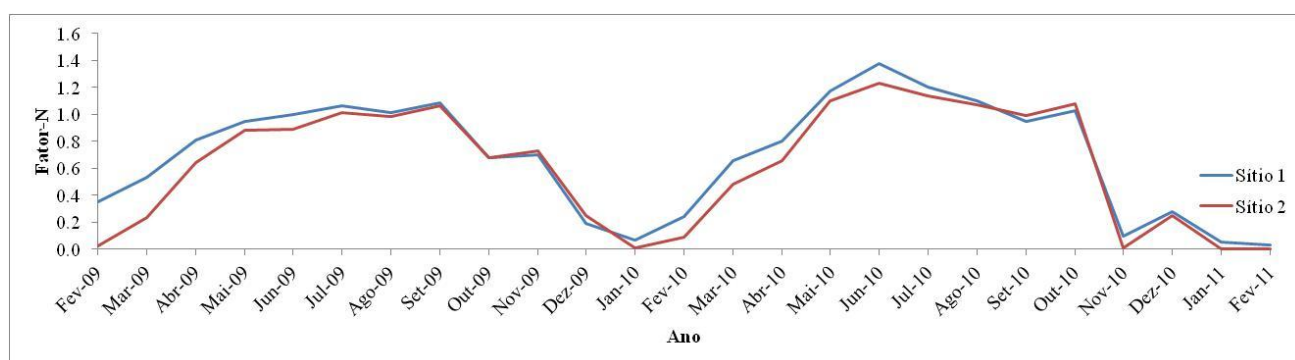


Fig. 5. Cálculo do Fator-N para os Sítios 1 e 2. Foram utilizadas profundidades de 10 cm para o FDDs por ser a profundidade mais próxima da superfície.

4. CONCLUSÕES

- A deposição de guano no Sítio 1, localizado em área de pinguineira ativa, representa importante fator para maiores resultados de *Thawing Degree Days* decorrentes de intensa atividades dos pinguins e reações químicas provocadas pela decomposição do guano.
- No Sítio 2, localizado na borda da pinguineira ativa e em uma posição mais baixa na encosta, que provavelmente favoreceu a maior espessura e ocorrência de neve por mais tempo, as maiores médias mínimas de temperatura evidenciam a capacidade de isolamento térmico da neve e a diferenciação microclimática decorrente do ambiente onde ocorrem, e que consequentemente resultou em resultados de *Freezing Degree Days* maiores do que os encontrados no Sítio 1.
- O maior acúmulo de neve no Sítio 2 refletiu nos menores resultados do Fator-N neste sítio, indicando ser este um parâmetro importante nas relações térmicas existente entre o solo e a camada de ar imediatamente acima.

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CHAPTER 3

Soil formation, classification and distribution in Hope Bay, Antarctic Peninsula

ABSTRACT

PEREIRA, Thiago Torres Costa. **Soil formation, classification and distribution in Hope Bay, Antarctic Peninsula**. Viçosa: UFV, 2012. Cap. 3 (Tese – Doutorado em Solos e Nutrição de Plantas).

Antarctic soils are formed on restricted areas that sum up about 0.32 %, or 45,000 km² of the continent, in ice-free coastal areas and glacial valleys between mountain ranges. Despite increased research in recent years, few studies on soil and permafrost in the Antarctic focused the peninsular area, where transitions climates occur between the wetter South Shetlands and dry Weddell Sea sector. We describe the morphological, physical, chemical, and mineralogical data on twelve representative soils of Hope Bay, emphasizing the processes of soil formation, and present their classification and mapping according USDA Soil Taxonomy and World Reference Base (WRB) system. Results showed that soils in Hope Bay are, in general, dystrophic, shallow, rocky, moderate to weak structural development, with low chroma, and cryoturbic. XRD peaks at 0.72 nm and 0.35 nm, characteristic of kaolinite, indicates former favorable conditions for greater chemical weathering compared with the current environment, which is subjected to the process of phosphatization on a previously weathered source material of sedimentary nature. Very high levels of P (Mehlich-1) and of some heavy metals, mainly total Cd and Pb, in areas of ruins, indicate anthropization and soil contamination on previous ornithogenic soil suggesting the presence of Technosols. The occurrence of permafrost in the first 30 cm along almost the whole extension of Hope Bay has a strong regulating effect on soil leaching and development processes. Along with phosphatization, permafrost appears to be the main process of cryopedogenesis involved in soil formation at this site. The soil areas were quantified according to the soil map: Ornithogenic Haplohemist (4.13 ha); Typic Haploturbel (10.03 ha); Lithic

Haploturbel (177.02 ha); Ornithogenic Haploturbel (145.12 ha) and association of Ornithogenic (Anthropic) Haploturbel + Ornithogenic Gelorthent (38.95 ha). Classification and mapping separated two main soil areas in Hope Bay: Ornithogenic Gelisols (Cryosols) in the lower parts, usually up to 60 m high, and Lithic Gelisols (Cryosols) above 60 m asl.

RESUMO

PEREIRA, Thiago Torres Costa. **Formação, classificação e mapeamento de solos em Hope Bay, Península Antártica**. Viçosa: UFV, 2012. Cap. 3 (Tese – Doutorado em Solos e Nutrição de Plantas).

Solos da Antártica são formados em áreas livres de gelo costeiras e vales glaciais entre cadeias de montanhas, representando 0,32 %, ou 45.000 km² do continente. A respeito do aumento das pesquisas nos últimos anos, poucos estudos em solos e permafrost na Antártica focaram na área peninsular, onde transições climáticas ocorrem entre as Ilhas Shetlands do Sul, úmidas, e o Mar de Weddell, seco. Estudos morfológicos, físicos, químicos e mineralógicos foram realizados em dezoito perfis representativos de solos de Hope Bay, enfatizando seus processos de formação, classificação e mapeamento destes solos, conforme os critérios da *Soil Taxonomy* e *WRB*. Os resultados mostraram que os solos são em geral distróficos, rasos, rochosos, possuem fraco ou moderado desenvolvimento estrutural, pouco cromados, e muito crioturbados. Difrátogramas de raio-X com picos em 0,72 nm e 0,35 nm, característicos da caulinita, indicam condições mais favoráveis à alteração química no passado, quando comparadas com o ambiente atual, sendo sugestivo o processo de fosfatização sobre material previamente alterado de natureza sedimentar. Teores muito elevados de P (Mehlich-1) e de metais pesados, principalmente Cd e Pb nas áreas de ruínas, indica antropização e contaminação do solo sobre sítio ornitogênico, sugerindo presença de Technosols. A ocorrência de permafrost nos primeiros 30 cm de profundidade em praticamente toda extensão de Hope Bay é um forte regulador da lixiviação e desenvolvimento dos solos. Desta forma, a fosfatização e o permafrost parecem ser os principais fatores envolvidos na criopedogênese e formação dos solos nestes sítios. As unidades de mapeamento quantificadas a partir do mapa de solos indicam: Organossolo Háptico hémico ornitogênico (4,13 ha); Gelissolo Háptico túrbico típico (10,03 ha); Gelissolo Háptico túrbico lítico (177,02 ha); Gelissolo Háptico túrbico ornitogênico (145,12 ha) e associação de Gelissolo Háptico túrbico (antrópico) ornitogênico + Neossolo gélico ornitogênico (38,95 ha). A classificação e mapeamento permitiram a separação de duas áreas principais em Hope Bay: Gelissolos (Criossolos) Ornitogênicos nas partes mais baixas, em torno de 60 de altitude, a Gelissolos (Criossolos) Líticos, superiores a 60 m de altitude.

1. INTRODUCTION

In Antarctica, soils are practically restricted to an area of 0.32 % the continent, extending over 45,000 km² of ice-free coastal areas and glacial valleys between mountain ranges (Bockheim, 1997; Bockheim and Ugolini, 2008).

From the beginning of soil observations in Antarctica, based on samples from the McMurdo region, collected in 1916 by Jensen during the British Antarctic Expedition (Bockheim and Ugolini, 2008), soil studies were restricted to the ice-free continental areas in which the soils are poorly developed and salts are accumulated along the pedon (Campbell and Claridge, 1987; Bockheim, 1997).

One issue discussed since the beginning of research on soil formation in Antarctica is whether the ice-free, very cold and dry areas, apparently without the possibility of proliferation of life, are modified by chemical weathering. However, several authors proved soil alterations and neoformation of clay minerals, even in the cold, dry environments of Antarctica (Bockheim and Ugolini, 2008), where substrates were obviously affected by pedogenetic processes.

Ugolini and Anderson (1973) observed ion migration even in frozen soils in cold and dry environments, and pointed out this fact as active in soil formation. More recently, Beyer et al. (1999), Beyer and Bolter (2000), Schaefer et al. (2004), Michel et al. (2006), Schaefer et al. (2008), and Simas et al. (2008), showed the occurrence of chemical changes in soils of Antarctica, sometimes beyond the expected.

First soil studies on the chemistry, mineralogy and microbiology were published by researchers in New Zealand (Bockheim and Ugolini, 2008) and the first soil map was produced by McCraw (1967) for Taylor Valley, in the south of Victoria Land. Although this was over 40 years ago, to date few soil maps were produced throughout the history of pedology in Antarctica (Bockheim and Ugolini, 2008).

In the 1960s, the main pedogenetic processes were recognized and the role of time in soil development (Ugolini, 1963). These processes included clay formation and acidification, salinization, redoximorphism, podsolization, and cryoturbation. This study resulted in a Special Series on Antarctic Research (Antarctic Soils and Soil Forming Processes) published by Tedrow and Ugolini in 1966, which proposed the first classification scheme for Antarctic soils, subdividing the Cold Desert soils

into six groups: Ahumic soils, Evaporite soils, Protoranker soils, Ornithogenic soils, Regosols and Lithosols (Bockheim and Ugolini, 2008).

In the 1980s, the International Permafrost Association (IPA) and the International Union of Soil Science (IUSS) formed the Cryosol Working Group that initiated efforts to improve the classification of permafrost soils. These efforts resulted in the establishment of the classes of Gelisols (Soil Taxonomy) and Cryosols (WRB).

Despite some publications in recent years, there are only few studies on soil and permafrost in the Antarctic Seas (Tatur, 1989; Bockheim and Ugolini, 1990, Blume et al., 2004, Schaefer et al., 2004, Michel et al. 2006), including the northern part of the Antarctic Peninsula, especially Hope Bay, where soil research is still incipient. Of the soil surveys in Maritime Antarctic, most focused on ornithogenic soils (Bockheim and Ugolini, 2008).

Soils of these areas are clearly different from those in other climatic zones of Antarctica for being more weathered and developed; the active layer tends to be deeper and vegetation more abundant, in response to higher temperatures and greater water availability (Campbell and Claridge 1987, Bockheim, 1997, Simas et al., 2006, Simas et al., 2007). However, comparing soils from the South Shetland Islands and Hope Bay, the latter were less developed, reflecting the lower average temperatures (less liquid water, even in summer) and leaching, with less diverse and distributed, often spaced vegetation.

The aimed of this study were to present morphological, physical, chemical, and mineralogical properties of soils at Hope Bay, Antarctic Peninsula; discuss the factors and processes involved in the soil formation; and classify and map soils, according to the classification systems Soil Taxonomy and the WRB, with some adaptations.

2. MATERIAL AND METHODS

2.1. Study area

The study was conducted in Hope Bay, in the Northern end of the Antarctic Peninsula. The study area is bordered in the South by Mount Flora (520 m asl) and in the East by the Buenos Aires glacier, whose snout reaches over 100 m. Scar (2002) defined the area of Mount Flora and surroundings as an Antarctic Specially Protected Area (ASPA 148). Excluding Mount Flora, the ice-free area between the sea and the glaciers covers a region of approximately 3 km², with average elevations of ≤ 100 m (Birkenmajer, 1993a, Martin-Serrano et al., 2005).

According to Köppen's classification, the region is part of the EF (polar) climate. The average temperature of Hope Bay measured at Esperanza Station, between 1952 and 2010 was -5.1 °C, with annual precipitation of approximately 150 mm, characterizing a semi-desert climate.

The geology of Hope Bay is composed of a metasedimentary (Trinity Peninsula Group - Hope Bay Formation: marine siliciclastic turbidites and sandstones), sedimentary (Botany Bay Group - Mount Flora Formation: sandstones, conglomerates and schists) and volcanic rock sequences (Antarctic Peninsula Volcanic Group - Kenney Glacier Formation: rhyolite-dacites, ignimbrites, conglomerates and cemented tuff) (Birkenmajer 1993b; del Valle et al. 2001; Scar, 2002).

The geomorphology is related to both paraglacial and periglacial processes and landforms, reflecting the widespread late Quaternary retreat of glaciers (Martín-Serrano et al., 2005), with shorter intervals of minor glacial advances. Most geomorphic processes are related to the coastal environmental, with persistent winds, summer melting, and increasing periglacial erosion, specially thermokarst features.

2.2. Soil sampling and soil mapping

Twelve pedons were described and sampled based on criteria established by Antarctic Permafrost and Soils (ANTPAS, 2006). Soils was classified according with USDA Soil Taxonomy (Soil Survey Staff, 2010) and World Reference Base for Soil

Resources (WRB) (ISSS Working Group, 2006), with some adaptations (Fig. 1). For detailed soil mapping, we used free pathway method (Embrapa, 1995). The cartographic reference material consisted of Quickbird image on 1:4,500 scale. The software used was ArcGIS 9.3 (ESRI, 2009) for data processing and map editing.

2.3. *Physical, chemical and mineralogical analysis*

Were determined the granulometry of soils, with adaptations for clay dispersion (Ruiz, 2005). With regards to the chemical analyses, soil pH was determined in distilled water and 1 mol L⁻¹ KCl solution; total organic carbon (TOC) (Yeomans and Bremner, 1988); available P, Na⁺ and K⁺ exchangeable were determined after extraction with 0.5 mol L⁻¹ HCl + 0.0125 mol L⁻¹ H₂SO₄ (Mehlich-1); Ca²⁺, Mg²⁺ and Al³⁺ by titration after extraction with 1 mol L⁻¹ KCl; potential acidity (H + Al) by titration after extraction with 0.5 mol L⁻¹ Ca(CH₃COO₂) at pH 7.0. All chemical analyses complied with SSSA (1996) and Embrapa (1997).

The total digestion of the ground and sieved (0.25 mm mesh) fine earth (< 2 mm) was carried out by a HCl, HNO₃ and HF digestion, performed in a microwave oven (CEM/MDS 2000) according to the EPA method 3052 (USEPA, 2011). The total amounts of Ca, Mg, K, Fe, Al, Mn, P, Cu, Zn, Cd, As, Cr, and Pb were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES).

The minerals in the total air-dried soil were identified by X-ray diffraction (XRD). For the clay fraction, the following treatments were performed: Fe-removal by dithionite-citrate-bicarbonate (DCB) (Mehra and Jackson, 1960); saturation with 1.0 mol L⁻¹ KCl; heating in an oven at 350 °C and 550 °C for 3 hours each; saturation with 1.0 mol L⁻¹ MgCl and glycerol solvation. A diffractometer (PANalytical / X'Pert Pro) was used, with CoK α radiation in the range between 4 and 50 °2 θ , at intervals from 0.017 °2 θ to 1 step s⁻¹, at a voltage of 40 kV and current of 30 mA. The interpretation of XRD data was based on Bish and Post (1989).



Ornithogenic Haploturbel - Turbic Cryosol (Ornithic)



Ornithogenic Gelorthent
Haplic Regosol (Ornithic)



Ornithogenic (Anthropic) Haploturbel
Turbic Technic Cryosol (Ornithic)



Lithic Haploturbel
Turbic Cryosol (Lithic)

Fig. 1. Illustration of representative pedons at Hope Bay, Antarctic Peninsula.

3. RESULTS AND DISCUSSION

3.1. Soils morphological and physical properties

In general, all soils have moderate or weak structural development, varying primarily between subangular blocky and granular (Table 1).

The formation of granular structure of Gelisols (Cryosols) is attributed to the freezing/thawing differential and ultradissection of the fine soil particles during freezing (Schaefer et al. 2004; van Vliet-Lan   et al., 2004). According to Bockheim and Tarnocai (1998), the blocky or granular structures at the surface and solid-looking subsurface materials are gelic material typical of cryopedogenesis.

Soils classified as ornithogenic (see classification) have clear or gradual transition from surface to subsurface horizons, with a darker to grayish surface horizon with higher organic matter, and bleached phosphatic B and/or C horizon, down the pedon. In non-ornithogenic soils (Typic Haploturbel) on the other hand the differentiation between horizons is not clear because of the lack of organic input, with little or no vegetation, and absence of phosphatization in the soils. Soils colonized by penguins are more developed than those without ornithogenesis, which highlights the importance of organisms in the local soil formation.

All soils vary from gravelly to very gravelly (on average 47 %), except for Histosol (HB5). The clay content was on average 16 dag kg⁻¹ (Table 1). Higher clay levels were observed in ornithogenic soils, probably due combination of warmer period in the past, when neoformation of secondary phosphate minerals reached lower depths, supported currently by rise of permafrost. Different results were observed by Simas et al. (2008) for ornithogenic soils, who suggested acidolysis as cause of the clay degradation, reducing clay levels in soils.

Table 1. Some morphological and physical properties of the studied soils

Pedon	Depth (cm)	Structure ¹	Transition	Color (dry)	Skel ² -----dag kg ⁻¹ -----	Sand	Silt	Clay
HB1 - Ornithogenic Haploturbel								
A1	0-8	w m bl/md m gr	clear wavy	7.5YR 4/2	65	62	21	17
B2	30-45/50	w m gr	clear flat	10YR 5/4	47	53	27	20
C	90-130+	w m gr/ma	diffuse/irregular	2.5Y 6/2	54	91	6	3
HB4 - Ornithogenic Haploturbel								
A	0-10	st m gr	gradual wavy	10YR 5/3	48	44	38	18
B	20-40	st m gr	gradual irregular	10YR 5/4	71	51	31	18
HB5 - Ornithogenic Haplohemist								
O	0-30	st m gr	-	5Y 3/2	0	11	58	31
HB6 - Ornithogenic Haploturbel								
A	0-5	w m bl	clear wavy	5Y 5/1	37	55	25	20
2C2	85-120	w f m bl/w m gr	-	5Y 6/2	41	64	26	10
HB9 - Typic Haploturbel								
A	0-15	md m gr	gradual wavy	2.5Y 6/4	41	37	39	24
HB10 - Ornithogenic Haploturbel								
A	0-10	w m bl	gradual wavy	10YR 6/3	60	24	37	39
B2	45-90	w m b bl/w m gr	gradual wavy	2.5Y 7/3	55	27	32	41
HB11 - Ornithogenic Gelorthent								
A	0-10	w m bl/sg	clear wavy	2.5Y 6/2	58	88	7	5
3Ax	35-60	md m gr/sg	clear wavy	2.5Y 6/3	62	94	3	3
3Cx	60-85	md m gr/sg	clear wavy	2.5Y 6/4	26	97	1	2
4A	85-120	sg	clear flat	2.5Y 6/2	73	94	4	2
HB15 - Ornithogenic (Anthropic) Haploturbel								
A	0-18	sg	clear flat	2.5Y 4/1	81	82	10	8
C2	27-60	w f gr/sg	-	2.5Y 7/1	43	55	30	15
HB17 - Ornithogenic Haploturbel								
A	0-10	-	abrupt flat	5Y 5/3	25	33	47	20
AB	10-15	-	-	5Y 5/1	40	35	44	21
2A	35-43	-	-	5Y 6/2	39	68	20	12
3A	60-72	-	-	5Y 6/2.5	33	49	28	23
HB19 - Lithic Haploturbel								
A	0-10	md m gr	diffuse irregular	-	27	52	45	3
C	30-60	w m bl/w m gr	-	-	36	53	45	2
HB20 - Ornithogenic Haploturbel								
A	0-13	md f m bl/sg	gradual irregular	5Y 6/2	55	54	31	15
C2	42-63	md f m bl/md m gr/sg	gradual irregular	5Y 6/3	36	64	25	11
HB21 - Lithic Haploturbel								
A	0-15	md m gr/sg	gradual wavy	2.5Y 6/4	52	76	13	11
C	15-40	w m bl/w m gr	-	2.5Y 6/5	36	80	13	7

¹ Development: w = weak, md = moderate, st = strong. Size: f = fine, m = medium. Type: ma = massive, gr = granular, bl = subangular blocky, sg = single grain, cr = crumbs; ² Percent of particles > 2 mm.

In pedon HB11, though ornithogenic, the clay contents were lower, because this part of Hope Bay had been abandoned by the penguins a longer time ago. Secondly, because of the proximity to the sea, favoring the removal of finer pedon material, especially when its level was lower in the past, before the glacio-isostatic uplift caused by the retreat of Buenos Aires glacier.

In Hope Bay, permafrost was observed on 30 cm depth along almost its entire extension. According to Bockheim and Tarnocai (1998), conditions such as poor

drainage, increase silt, frequent freeze-thaw cycles, and permafrost down to 1 m are factors that favor cryoturbation (cryopedogenesis process).

Cryoturbation occurs in all soils, evidenced by presence of wedges and involutions, wavy/irregular transitions between soil horizons, as well for the erratic distribution of clay and silt along the pedon (Table 1). The only pedon without cryoturbation was HB5 (located on the banks of Boeckella lake - see Soil Map), since HB5 was formed more recently, from the downward development of thermokarst and lowering of the lake level. According to French (1996), the development of thermokarst was caused by the thermal imbalance of permafrost and increased depth of the active layer, induced, among other factors, by the local weather conditions. In this case, an increase in air temperature of $0.41\text{ }^{\circ}\text{C decade}^{-1}$ in the period 1961 to 2000, observed by Turner et al. (2005) in Hope Bay, can be the main factor for the lowering of permafrost and origin of thermokarst.

In and around pedon HB9, represented by the Five Lake Valley (see Soil Map), continued freeze/thaw cycles favored solifluction and formation of typical features such as soils with patterned grounds. Additionally, silty layers formation and expulsion of finest materials to the surface (frost heave) were observed not only in HB9, but in most pedons of Gelisols (Cryosols) studied.

Even areas with some stagnant water (HB5 and HB9), no redoximorphic features were observed, as described by Blume et al. (2002) and Simas et al. (2008) for some hydromorphic soils of the Maritime Antarctic. No features of salinization were observed either in any pedon studied, no podzolization, even in soils with high sand content, corroborating the pedogenetic zoning proposed by Bockheim and Ugolini (1990), and modified and extended by Blume et al. (1997). These observations confirm the transition status of Hope Bay to the so-called "polar desert".

3.2. Chemical properties

The studied soils are mostly dystrophic, with highest levels of Ca^{2+} and Mg^{2+} , followed by K^{+} and Na^{+} (Table 2).

Table 2. Chemical properties of the studied soils

Pedon	Depth (cm)	pH		Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Al ³⁺	H+Al	CEC	PBS	m ¹	Na ²	TOC	P
		H ₂ O	KCl												
HB1 - Ornithogenic Haploturbel															
A1	0-8	4.66	4.29	10.46	4.77	0.38	1.03	0.67	19.50	36.14	46.00	3.90	5.94	13.44	8675.80
B2	30-45/50	4.42	3.87	10.35	1.68	0.73	1.37	1.33	20.60	34.73	40.70	8.60	8.89	9.62	8059.80
C	90-130+	4.89	3.64	6.32	0.59	1.82	0.45	0.57	20.70	29.88	30.70	5.80	4.60	1.75	1296.10
HB4 - Ornithogenic Haploturbel															
A	0-10	5.25	4.89	10.00	2.23	0.21	1.68	0.29	23.30	37.42	37.70	2.00	11.63	11.05	7570.30
B	20-40	4.42	3.86	10.41	3.39	0.66	1.76	0.67	22.50	38.72	41.90	4.00	10.44	10.16	6728.80
HB5 - Ornithogenic Haplohemist															
O	0-30	4.96	4.50	5.20	1.12	0.20	0.47	0.10	9.10	16.09	43.40	1.40	6.57	9.28	2952.70
HB6 - Ornithogenic Haploturbel															
A	0-5	4.70	3.68	3.31	0.97	0.35	0.54	0.86	9.90	15.07	34.30	14.30	9.01	1.67	877.60
2C2	85-120	4.90	3.69	2.78	1.45	0.50	0.16	0.86	6.30	11.19	43.70	15.00	2.84	0.30	604.00
HB9 - Typic Haploturbel															
A	0-15	6.61	4.32	4.45	0.67	0.53	1.68	0.00	3.10	10.43	70.30	0.00	21.47	0.38	86.30
HB10 - Ornithogenic Haploturbel															
A	0-10	6.72	6.31	1.45	4.56	2.91	5.52	0.00	20.70	35.14	41.10	0.00	35.01	8.53	8326.50
B2	45-90	5.43	3.75	4.50	3.77	2.41	2.19	1.05	14.80	27.67	46.50	7.50	15.77	6.44	9314.60
HB11 - Ornithogenic Gelorthent															
A	0-10	4.80	3.37	1.73	0.66	0.53	0.88	0.86	9.10	12.90	29.50	18.50	18.80	1.23	920.10
3Ax	35-60	4.89	3.24	0.54	0.36	1.27	0.79	0.86	7.20	10.16	29.10	22.50	20.78	0.90	395.70
3Cx	60-85	4.91	3.16	1.10	0.39	1.29	0.66	0.86	8.80	12.24	28.10	20.00	15.35	0.74	630.30
4A	85-120	4.85	3.38	1.10	0.48	1.16	0.85	1.33	7.50	11.09	32.40	27.00	17.36	0.71	1683.80
HB15 - Ornithogenic (Anthropic) Haploturbel															
A	0-18	6.04	5.93	1.88	1.08	0.20	0.53	0.00	2.50	6.19	59.60	0.00	14.27	1.71	718.00
C2	27-60	4.81	3.45	1.22	0.81	0.15	0.23	2.00	9.40	11.81	20.40	45.40	5.29	0.46	454.70
HB17 - Ornithogenic Haploturbel															
A	0-10	7.28	6.65	1.51	12.43	0.73	1.55	0.00	10.70	26.92	60.30	0.00	9.55	8.70	10449.30
AB	10-15	6.46	5.92	1.45	8.37	0.75	0.71	0.00	5.70	16.98	66.40	0.00	6.20	3.77	4288.70
2A	35-43	7.18	6.59	0.85	7.64	0.76	0.21	0.00	4.40	13.86	68.30	0.00	2.24	1.12	1843.80
3A	60-72	6.93	6.33	2.47	6.77	0.89	0.20	0.00	2.80	13.13	78.70	0.00	1.97	0.92	860.20
HB19 - Lithic Haploturbel															
A	0-10	7.07	5.81	3.61	1.13	0.20	0.29	0.00	0.30	5.53	94.60	0.00	5.47	1.50	97.50
C	30-60	7.02	6.00	3.64	1.20	0.21	0.24	0.00	0.50	5.79	91.40	0.00	4.50	0.93	170.60
HB20 - Ornithogenic Haploturbel															
A	0-13	5.20	3.64	0.49	0.63	0.37	0.38	0.62	10.20	12.07	15.50	24.89	10.83	0.46	817.60
C2	42-63	4.87	3.60	0.37	0.55	0.23	0.27	1.19	9.00	10.42	13.60	45.59	7.56	0.46	736.60
HB21 - Lithic Haploturbel															
A	0-15	5.01	3.99	0.54	0.76	0.15	0.23	0.76	6.30	7.98	21.10	31.14	5.26	0.38	90.60
C	15-40	5.92	4.15	1.36	1.95	0.23	0.34	0.00	3.90	7.78	49.90	0.00	6.83	0.30	20.20

¹Al saturation; ²Na saturation.

The results are in agreement with findings of Schaefer et al. (2004) and Simas et al. (2008) for Gelisols (Cryosols) from the South Shetlands archipelago. Despite the high bases sum found in some soils, the dystrophic character can be related to the higher potential acidity (H+Al), possibly influenced by high organic matter enhancing acidity.

Lower pH values were observed for ornithogenic soils, which can be explained by acidification due microbial degradation of organic matter; organic carbon levels were higher in the ornithogenic pedons (on average 4.24 dag kg⁻¹). To the low pH, the values were higher than reported by Schaefer et al. (2004) and Simas et al. (2008) for ornithogenic soils of Admiralty Bay. In addition, the reduced base leaching in Hope Bay, due to the lower presence of liquid water in summer may have diminished the ability of soil acidification. These effects seem to have resulted in lower Al³⁺ values than those found by Schaefer et al. (2004), Simas et al. (2007) and Simas et al. (2008), whose studies involved pedogenetically more developed and more acidic soils.

Very high Mehlich-1 extractable P levels were found, so that all ornithogenic soils of Hope Bay were classified as "strongly ornithogenic" according to the criteria proposed by Simas et al. (2007). The P levels in pedon HB15 reaching 586.35 mg dm⁻³ evidence an anthropic process on ornithogenesis, since the former penguin colony became a basis for British installations in the past half century. Additionally, the nearby pedon HB11, also with high P levels (Mehlich-1), evidences the occurrence of phosphatization at these sites, and that the penguin rookery of Hope Bay covered a larger area in the past than now and was forced to retreat, most likely, by the secular human activity in the region.

Currently, aside from the human pressure, another factor restricting the large penguin colony to the central region of Hope Bay, is the development of thermokarst mentioned above, which acts as a physical barrier to the bird's movement. In view thereof, propose to the Scientific Committee on Antarctic Research, that the 148 ASPA should cover, as of this study, not only the area of Mount Flora, but also the current Penguin rookery, for their protection. As result, a higher environmental quality can be expected in this ice-free area, which, though small, hosts one of the largest, if not the largest penguin population in the northern part of the Antarctic Peninsula.

3.3. Total elemental composition

The total CaO, MgO and K₂O contents were, on average, 3.59 dag kg⁻¹, 0.68 dag kg⁻¹ and 2.44 dag kg⁻¹ for ornithogenic soils, respectively, and 1.71 dag kg⁻¹, 0.70 dag kg⁻¹ and 2.74 dag kg⁻¹ for the lithic soils, respectively (Table 3).

Table 3. Total concentrations in < 2 mm air-dried soil samples

Pedon	Depth (cm)	CaO	MgO	K ₂ O	Fe ₂ O ₃	Al ₂ O ₃	MnO	P ₂ O ₅
-----dag kg ⁻¹ -----								
HB1 - Ornithogenic Haploturbel								
A1	0 - 8	8.22	0.88	2.00	1.92	9.22	0.01	10.84
B2	30 - 45/50	9.10	0.81	1.88	2.61	9.20	0.05	13.42
C	90 - 130+	1.70	0.52	3.33	4.62	5.04	0.03	5.91
HB4 - Ornithogenic Haploturbel								
A	0 - 10	11.04	0.88	1.28	0.87	1.45	0.07	22.48
B	20 - 40	2.53	0.68	2.76	5.58	1.22	0.02	10.56
HB5 - Ornithogenic Haplohemist								
O	0-30	2.17	0.63	2.38	3.55	1.61	0.03	3.09
HB6 - Ornithogenic Haploturbel								
A	0 - 5	1.92	0.65	2.97	4.26	3.47	0.03	1.44
2C2	85 - 120	1.81	0.57	2.66	3.82	3.76	0.04	0.65
HB9 - Typic Haploturbel								
A	0 - 15	2.18	0.71	2.94	5.54	2.45	0.08	0.19
HB10 - Ornithogenic Haploturbel								
A	0 - 10	5.86	0.92	2.43	0.80	2.72	0.02	23.41
B2	45 - 90	5.91	0.72	2.62	3.20	3.18	0.02	19.79
HB11 - Ornithogenic Gelorthent								
A	0 - 10	1.79	0.57	2.76	3.43	4.36	0.02	2.26
3Ax	35 - 60	2.04	0.62	2.42	3.30	4.35	0.03	1.32
3Cx	60 - 85	1.88	0.59	2.62	2.83	4.64	0.02	2.23
4A	85 - 120	2.16	0.65	2.49	2.94	4.35	0.03	0.95
HB15 - Ornithogenic (Anthropic) Haploturbel								
A	0 - 18	1.82	0.60	2.01	13.61	2.53	0.06	0.73
C2	27 - 60	1.62	0.52	2.53	3.49	2.27	0.03	0.69
HB17 - Ornithogenic Haploturbel								
A	0 - 10	8.23	1.34	1.43	1.42	1.26	0.11	20.82
AB	10 - 15	2.15	0.63	2.44	4.16	4.17	0.06	2.38
2A	35 - 43	1.72	0.58	2.70	4.10	4.69	0.05	0.69
3A	60 - 72	1.76	0.59	2.74	4.59	4.32	0.06	0.62
HB19 - Lithic Haploturbel								
A	0 - 10	1.68	0.53	2.55	3.81	3.47	0.04	0.10
C	30 - 60	1.58	0.50	2.72	3.59	1.72	0.03	0.11
HB20 - Ornithogenic Haploturbel								
A	0 - 13	1.57	0.48	2.76	4.34	4.24	0.04	0.76
C2	42 - 63	1.89	0.61	2.54	3.70	0.96	0.03	0.48
HB21 - Lithic Haploturbel								
A	0 - 15	1.11	1.17	2.52	2.21	1.72	0.02	0.07
C	15 - 40	1.99	0.60	2.97	3.33	3.25	0.04	0.07

Similar results were found by Tatur (1989) for penguin rookeries surface samples in the same area, and by Guerra et al. (2011), who reported soil contamination by heavy metals.

Higher levels of CaO may be related to a reduced leaching of this element, favorable for the formation of phosphatic clays (Tatur, 1989). Moreover, plagioclases were detected in all soils (see mineralogy). In this case, the presence of easily weathered primary minerals in the clay fraction indicates a limited chemical weathering and cryoclasty effect decreasing the particle size, as suggested by Simas et al. (2006).

The higher total amount of K₂O compared with exchangeable amounts suggests that is present mostly in non-exchangeable forms, possibly associated with the formation of phosphate clays typical of the phosphatization process, as well as associated with the micaceous minerals and K-feldspar in the soil (see mineralogy). With regard to MgO, lower total levels and relatively higher proportion of exchangeable Mg²⁺ suggests a greater inputs of this element by penguins.

The P₂O₅ results were, on average, 6.61 dag kg⁻¹ for ornithogenic soils (Table 3), and 0.11 dag kg⁻¹ for the lithic soils. The P enrichment at the sites to former or current ornithogenesis is relevant, since the parental materials in Hope Bay are chemically poor.

The average total contents of Fe₂O₃ and Al₂O₃ were 3.78 and 3.77 dag kg⁻¹, respectively, for the ornithogenic soils, and 2.52 and 3.70 dag kg⁻¹, respectively, for the lithic soils. This reveal that these oxides are closely related to the parent material. However, the somewhat higher total Al₂O₃ contents at ornithogenic than at non-ornithogenic sites (lithic soils) suggests a greater precipitation of this oxide from phosphatic clays.

The total heavy metal contents were on average 28.13 mg kg⁻¹ (As), 5.96 mg kg⁻¹ (Cd), 53.69 mg kg⁻¹ (Cr), 125.32 mg kg⁻¹ (Cu), 32.19 mg kg⁻¹ (Pb), and 244.62 mg kg⁻¹ (Zn) (Table 4).

All values exceeded the soil quality reference levels indicated by Chen et al. (1991): 5.20 mg kg⁻¹ (As), 1.60 mg kg⁻¹ (Cd), 37.00 mg kg⁻¹ (Cr), 17.00 mg kg⁻¹ (Cu), 16.00 mg kg⁻¹ (Pb), and 48.00 mg kg⁻¹ (Zn).

Specifically for pedon HB15 (not used in average), Cd and Pb levels were 75.23 mg kg⁻¹ and 974.46 mg kg⁻¹, respectively, in horizon A. Very high metal contents found in this pedon are related to the charred materials of diverse nature

found and are related to the ruin at the site. At the most contaminated anthropic sites in Hope Bay, very high semi-total levels were observed by Guerra et al. (2011), with 47.00 mg kg⁻¹ (Cd) 19,381.00 mg kg⁻¹ (Pb), and 5,225.00 mg kg⁻¹ (Zn). According to these authors, these elements contaminated the soil most, and are systematically related to the secular human activity at the area.

Table 4. Total concentrations of heavy metals in < 2 mm air-dried soil samples

Pedon	Depth (cm)	Cu	Zn	Cd	As	Cr	Pb
-----mg kg ⁻¹ -----							
HB1 - Ornithogenic Haploturbel							
A1	0 - 8	272.47	420.84	3.88	25.62	58.30	16.67
B2	30 - 45/50	266.11	422.71	5.46	33.04	75.11	25.55
C	90 - 130+	176.46	158.89	7.62	36.05	58.87	49.22
HB4 - Ornithogenic Haploturbel							
A	0 - 10	346.39	837.79	5.83	31.66	28.15	16.94
B	20 - 40	249.66	292.75	6.56	15.92	44.63	25.24
HB5 - Ornithogenic Haplohemist							
O	0-30	228.84	207.15	5.22	24.79	35.96	39.31
HB6 - Ornithogenic Haploturbel							
A	0 - 5	83.67	85.68	5.01	27.07	64.14	36.19
2C2	85 - 120	43.76	98.88	4.53	29.38	29.96	28.49
HB9 - Typic Haploturbel							
A	0 - 15	58.82	178.57	6.48	57.98	45.08	41.17
HB10 - Ornithogenic Haploturbel							
A	0 - 10	283.03	862.58	3.41	28.13	15.98	5.04
B2	45 - 90	244.24	947.44	7.28	20.42	34.29	25.20
HB11 - Ornithogenic Gelorthent							
A	0 - 10	46.85	63.60	4.70	20.43	79.72	22.51
3Ax	35 - 60	37.65	59.13	4.86	36.90	59.95	26.48
3Cx	60 - 85	42.39	76.78	4.66	24.58	61.12	30.23
4A	85 - 120	35.91	57.73	5.45	39.62	55.42	39.16
HB15 - Ornithogenic (Anthropic) Haploturbel							
A	0 - 18	146.61	457.16	75.23	15.41	101.65	974.46
C2	27 - 60	32.04	61.34	62.13	19.98	55.54	37.00
HB17 - Ornithogenic Haploturbel							
A	0 - 10	422.39	588.47	9.25	29.92	34.74	34.02
AB	10 - 15	98.49	146.50	10.65	36.79	53.80	54.64
2A	35 - 43	37.06	78.61	9.33	38.67	63.05	52.01
3A	60 - 72	37.61	78.43	8.29	25.22	56.51	39.82
HB19 - Lithic Haploturbel							
A	0 - 10	33.95	77.18	7.46	24.35	62.00	36.32
C	30 - 60	37.44	73.30	4.82	13.99	62.66	25.88
HB20 - Ornithogenic Haploturbel							
A	0 - 13	38.67	75.16	7.17	38.88	55.39	48.58
C2	42 - 63	39.52	85.74	4.17	28.72	57.48	26.87
HB21 - Lithic Haploturbel							
A	0 - 15	18.20	44.89	2.12	13.23	50.85	20.76
C	15 - 40	25.37	67.55	4.89	22.84	49.17	38.57

3.4. Mineralogical properties

The X-ray diffraction patterns confirm the presence of clays mineral assemblage typical of the phosphatization process: taranakite, minyulite, leucophosphate, struvite and fluorapatite (Fig. 2).

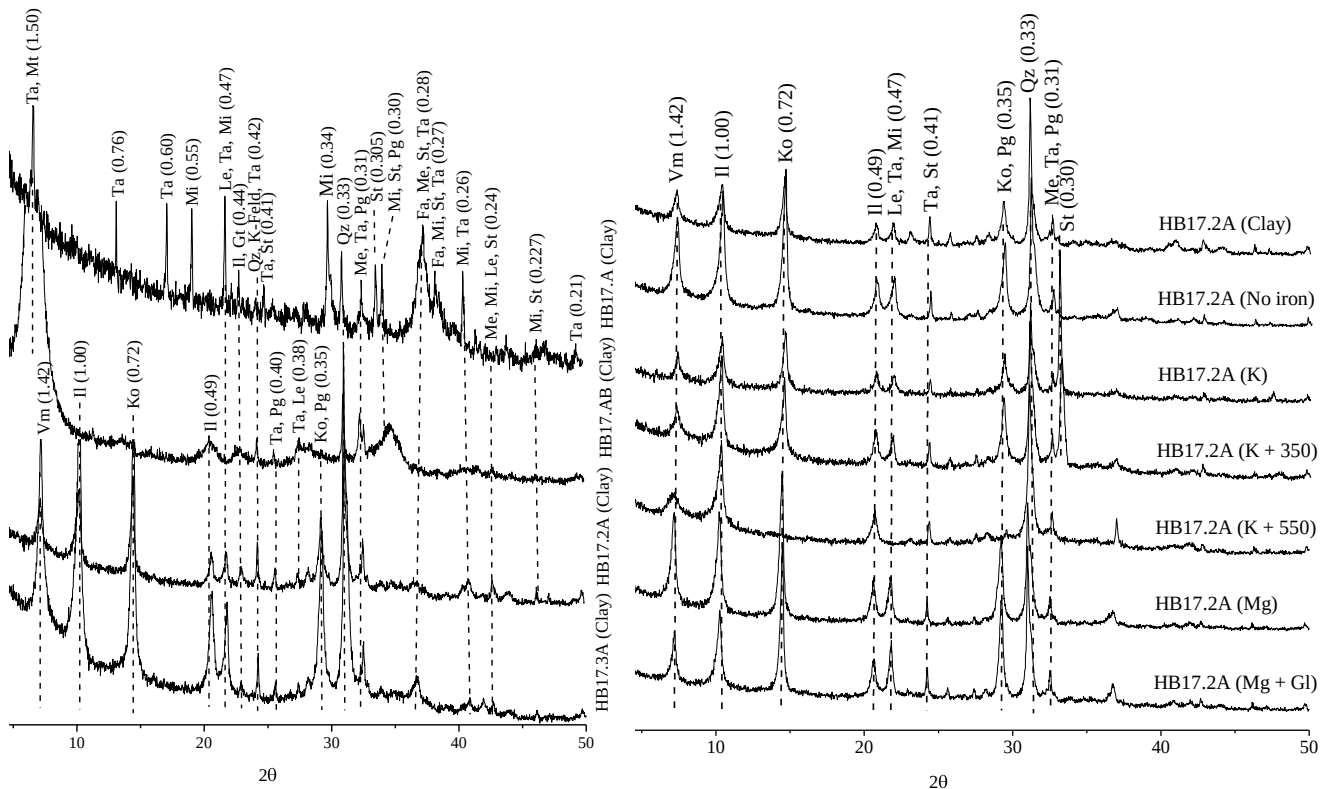


Fig. 2. XRD patterns for the ornithogenic soils of Hope Bay, Antarctic Peninsula. Pedon HB17 (clay and treatments). Mt – montmorillonite, Ko – kaolinite, Ta – taranakite, Le – leucophosphate, Mi – minyulite, St – struvite, Fa – fluorapatite, Me – metavariscite, Qz – quartz, K-Feld – K-feldspar, Pg – plagioclase, Mc – mica. “d” spacing in nm.

According to Barczuk and Tatur (2003), they are the result of very reactive and supersaturated percolating guano. At the ornithogenic sites of Hope Bay, these are the predominant minerals of clay fraction.

XRD peaks at 1.50, 1.42 and 1.00 nm indicated the presence of the clay minerals montmorillonite, vermiculite and illite, respectively. In the treatments (Fig. 2), it was observed that after KCl saturation and heating to 550 °C, vermiculite was partly maintained at 1.42 nm, not completely collapsing to 1.00. This may be related to either situations: the occurrence of hydroxy-Al interlayered 2:1 clay minerals, making it difficult to decrease in the “d” spacing between the atomic planes; and 2:1

clay minerals without Al- hydroxyl interlayers, due to the competition on the part of Al for phosphates and organic matter-bound Al.

XRD peaks at 0.42, 0.31 and 0.30 nm indicate the presence of K-feldspar and plagioclase in the clay fraction, possibly related to lower bases and Si leaching, contributing to low chemical alteration in the thermodynamic equilibria involving Ca, Mg and K. Apart from these minerals, the presence of quartz was also detected in all soils, due to the reduced dissolution ability in the environment, associated with strong cryoclasty, favoring the mineral fragmentation and its detection in clay fraction.

In the treatments of the clay fraction, the presence of kaolinite was confirmed by the disappearance of XRD peaks at 0.72 nm and 0.35 nm after heating to 550 °C (Fig. 2). Kaolinite in Antarctic soils is rather unusual, although it has been detected by Blume et al. (2002) and Simas et al. (2008) in soils of the coastal regions of Antarctica. Since the nature of the parent material of the soil of this study was sedimentary, pre-weathered and chemically poor, it seems that phosphatization occurred on previously altered material, perhaps in an environment with more favorable past conditions for chemical alterations and mineral transformation.

Phosphate minerals were also found in the silt fraction of the ornithogenic soils, in similar amounts (Fig. 3).

Therefore, taranakite, minyulite, leucophosphite, struvite, and fluorapatite, are found in minute microaggregates, as illustrated by Schaefer et al. (2008). The same was observed for the coarse and fine sand fractions, which apparently have similar behavior in terms of mineral occurrence, including the presence of the same phosphate minerals, as well as metavariscite (XRD peaks at 0.24, 0.28 and 0.31 nm) (Fig. 3).

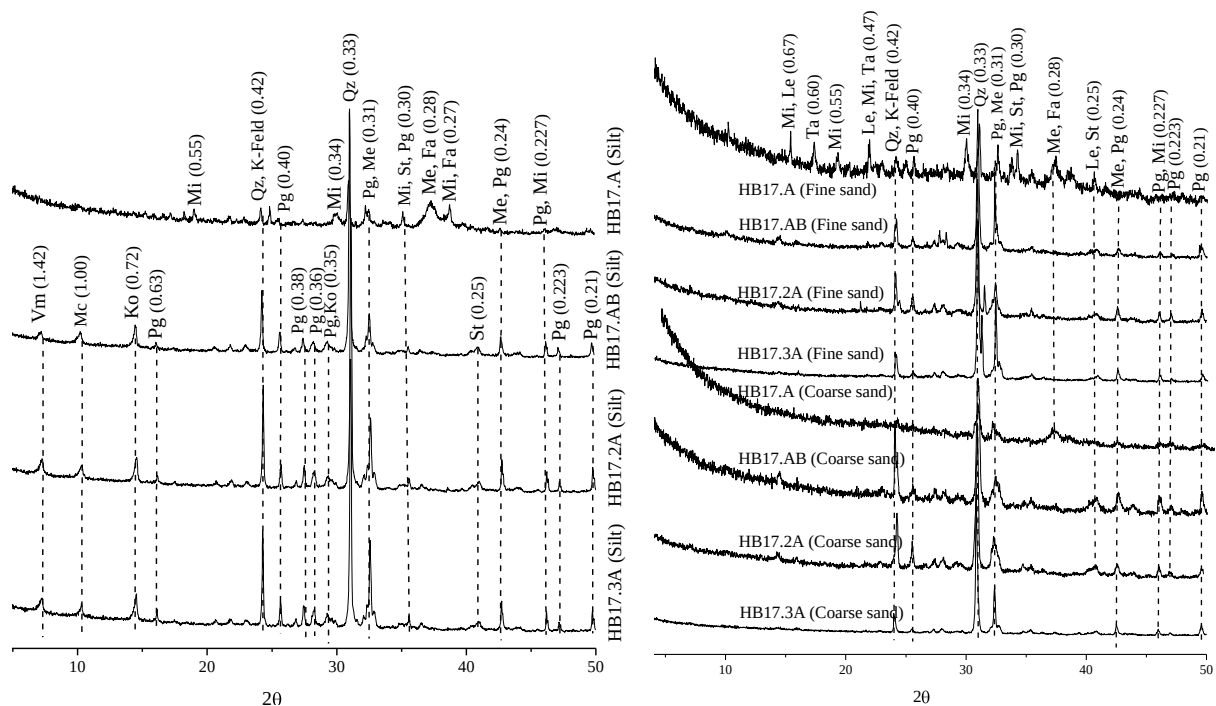


Fig. 3. XRD patterns for the ornithogenic soils of Hope Bay, Antarctic Peninsula. Pedon HB17 (silt and sand). Mt – montmorillonite, Vm – vermiculite, Il – illite, Ta – taranakite, Le – leucophosphite, Mi – minyulite, St – struvite, Fa – fluorapatite, Me – metavariscite, Ko – kaolinite, Gt – goethite, Qz – quartz, K-Feld – K-feldspar, Pg – plagioclase, Mc – mica. “d” spacing in nm.

In pedon HB21, representative of Lithic Haploturbels (Turbic Cryosols - Lithic), vermiculite, illite, kaolinite, and plagioclase were detected in the clay fraction (Fig. 4).

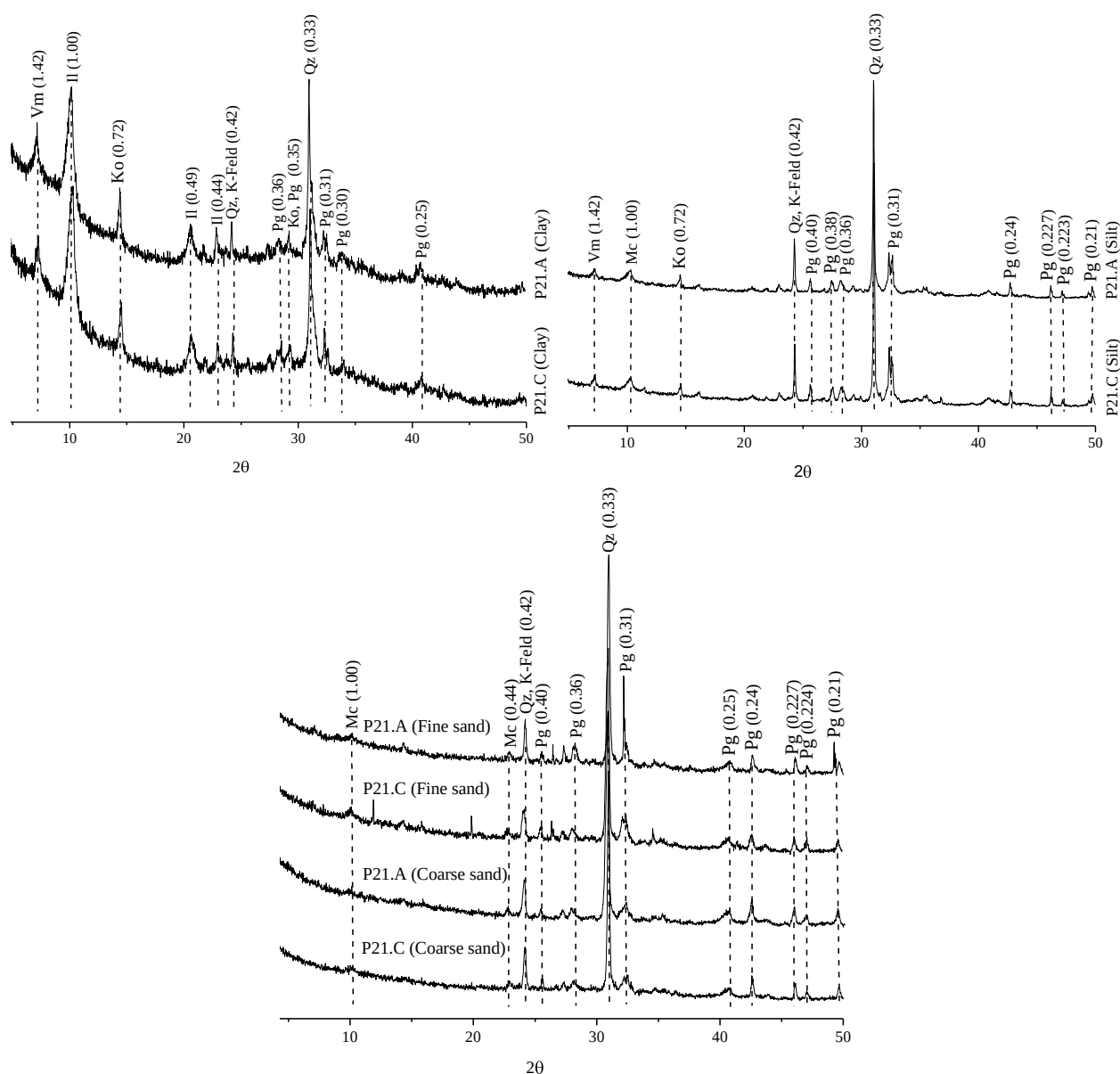


Fig. 4. XRD patterns for the some Gelisols (Cryosols) of Hope Bay, Antarctic Peninsula. Pedon HB21 (clay, silt and sand). Vm – vermiculite, Il – illite, Ko – kaolinite, Qz – quartz, K-Feld – K-feldspar, Pg – plagioclase, Mc – mica. “d” spacing in nm.

In the silt and sand fractions of lithic soils mainly, aluminosilicates and quartz were detected, indicating chemical poverty of the parental material (Fig. 4).

3.5. Soil classification and mapping

The soils were classified according to criteria developed by Soil Survey Staff (2010) and ISSS Working Group (2006), as shown in Table 5.

Table 5. Actual and adapted classification for studied soils at Hope Bay, Antarctic Peninsula

Pedon	Soil Taxonomy	Soil Taxonomy*
HB1	Typic Haploturbel	Ornithogenic Haploturbel
HB4	Typic Haploturbel	Ornithogenic Haploturbel
HB5	Typic Haplohemist	Ornithogenic Haplohemist
HB6	Typic Haploturbel	Ornithogenic Haploturbel
HB9	Typic Haploturbel	-
HB10	Typic Haploturbel	Ornithogenic Haploturbel
HB11	Typic Gelorthents	Ornithogenic Gelorthent
HB15	-	Ornithogenic (Anthropic) Haploturbel
HB17	Typic Haploturbel	Ornithogenic Haploturbel
HB19	Lithic Haploturbel	-
HB20	Typic Haploturbel	Ornithogenic Haploturbel
HB21	Lithic Haploturbel	-
Pedon	WRB	WRB*
HB1	Turbic Cryosol (Ornithic, Dystric, Skeletic)	-
HB4	Turbic Cryosol (Ornithic, Dystric, Skeletic)	-
HB5	Hemic Histosol (Ornithic, Gelic, Dystric)	-
HB6	Turbic Cryosol (Ornithic, Dystric, Skeletic)	-
HB9	Turbic Cryosol (Eutric, Oxyaquic, Skeletic)	-
HB10	Turbic Cryosol (Ornithic, Dystric, Skeletic)	-
HB11	Haplic Regosol (Ornithic, Gelic, Dystric, Skeletic)	-
HB15	Turbic Technic Cryosol (Ornithic, Skeletic)	-
HB17	Turbic Cryosol (Ornithic, Eutric, Skeletic)	-
HB19	Turbic Cryosol (Dystric)	Turbic Cryosol (Lithic, Dystric)
HB20	Turbic Cryosol (Ornithic, Dystric, Skeletic)	-
HB21	Turbic Cryosol (Dystric)	Turbic Cryosol (Lithic, Dystric)

*Adapted classification.

The prefix "ornithogenic" was adapted for the USDA Soil Taxonomy to an enhanced applicability of this classification system to the reality of studied soils. This suggestion was also proposed by Simas et al. (2007) for ornithogenic soils in Maritime Antarctic. In addition to this prefix, the term "anthropic" was added for pedon HB15, which is a Gelisol (Cryosol), because this has a pedogenetic process that involves anthropization on ornithogenesis.

The suffix "lithic" was adapted for WRB system at pedon HB19 and HB21, which represent a large Lithic Haploturbel area (Turbic Cryosol - Lithic) observed in Hope Bay (Fig. 5).

Results of soil mapping were Ornithogenic Haplohemist (4.13 ha); Typic Haploturbel (10.03 ha); Lithic Haploturbel (177.02 ha); Ornithogenic Haploturbel (145.12 ha) and association of Ornithogenic (Anthropic) Haploturbel + Ornithogenic Gelorthent (38.95 ha) (Fig 5). Rocky coast and beach cover 30.83 ha.

The highest proportion of Gelisols (Cryosols) in Hope Bay inferred from the soil map is related to shallow and practically uninterrupted permafrost along the entire bay length.

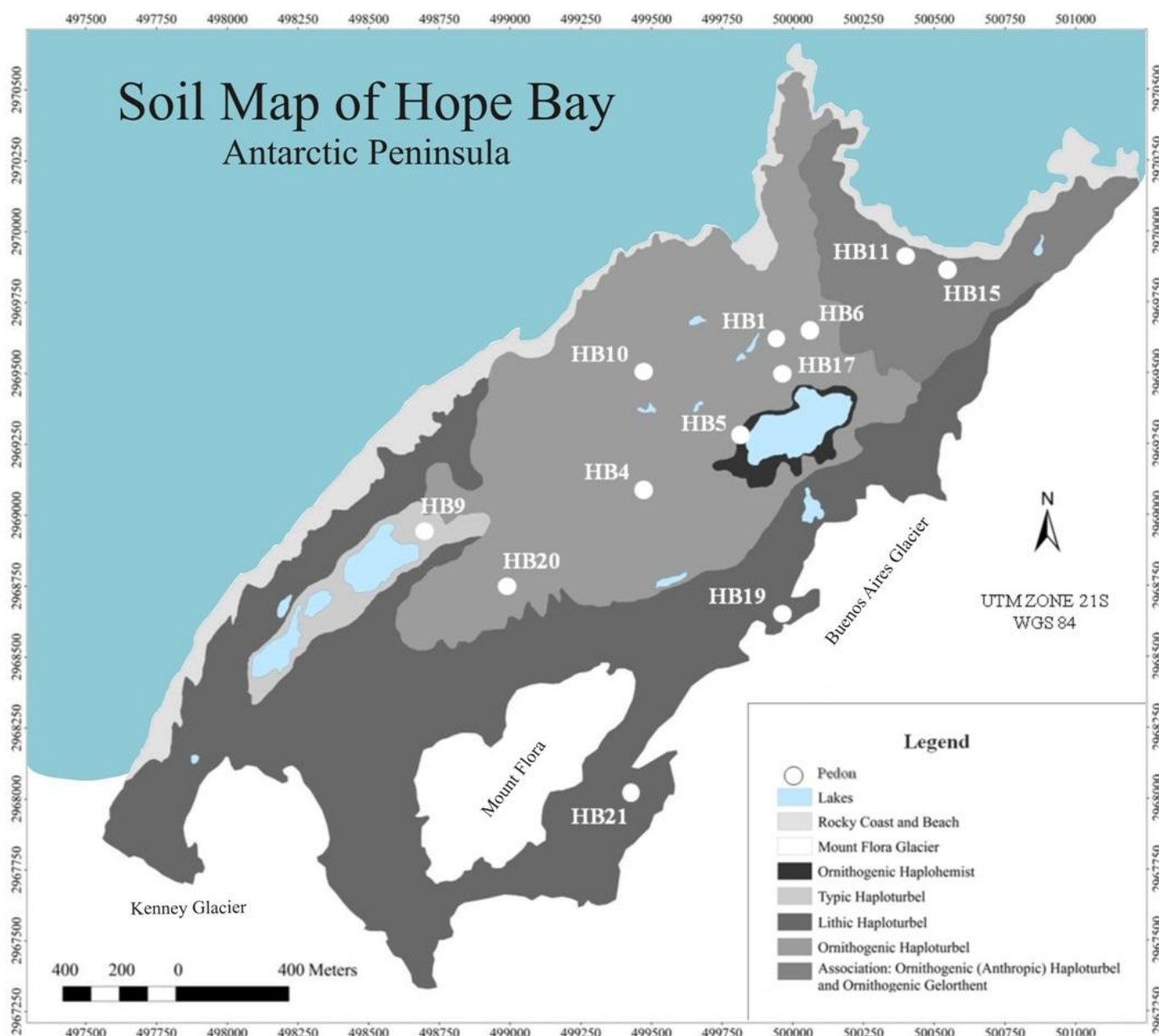


Fig. 5. Soil Map of Hope Bay, Antarctic Peninsula. Adapted classification for soils studied (adapted from Soil Survey Staff, 2010). To download this map, access the website <www.terrantar.com.br>.

Results indicate that soils influenced by ornithogenesis cover occur not only in areas of Ornithogenic Haploturbels (Turbic Cryosols - Ornithic), but also in associated soil areas shown in Fig. 5.

Despite some differences between pedons, regarding, e.g., texture and PBS, inside of "Ornithogenic Haploturbels (Turbic Cryosols - Ornithic)", it was decided to maintain pedons HB1, HB4, HB6, HB10, HB17, and HB20 in this unit because involve similarities with color, structure, cryoturbation, high P (Mehlich-1) and P_2O_5 levels, and clay mineralogy, mainly.

According to the Soil Map, field information and analytical data, Hope Bay can be separated into two main soil areas: ornithogenic soils in the lower parts, usually to an altitude of 60 m asl, and lithic soils above 60 m asl.

4. CONCLUSIONS

- Soils of Hope Bay are, in general, dystrophic, shallow, rocky, with moderate to weak structural development, poorly chromic, and cryoturbated;
- In Hope Bay, XRD peaks at 0.72 nm and 0.35 nm, characteristic of kaolinite, indicate a past more favorable to chemical weathering and mineralogical transformations. The current environment is subjected to the phosphatization process on previously weathered material of sedimentary nature;
- The occurrence of permafrost on 30 cm depth along almost extension of Hope Bay has a strong regulating effect on soil leaching and development processes. Associated with phosphatization, permafrost appears to be the main cryopedogenesis process involved in soil formation at this area;
- According to the Soil Map, the area was separated: Ornithogenic Haplohemist (4.13 ha); Typic Haploturbel (10.03 ha); Lithic Haploturbel (177.02 ha); Ornithogenic Haploturbel (145.12 ha) and association of Ornithogenic (Anthropic) Haploturbel + Ornithogenic Gelorthent (38.95 ha);
- Based on soil classification and soil mapping, two main areas were separated in Hope Bay: ornithogenic soils in the lower parts, usually to an altitude of 60 m, and lithic soils above 60 m asl.

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CHAPTER 4

Genesis, mineralogy and ecological significance of ornithogenic soils from a semi-desert polar landscape at Hope Bay, Antarctic Peninsula

ABSTRACT

PEREIRA, Thiago Torres Costa. **Genesis, mineralogy and ecological significance of ornithogenic soils from a semi-desert polar landscape at Hope Bay, Antarctic Peninsula.** Viçosa: UFV, 2012. Cap. 4 (Tese – Doutorado em Solos e Nutrição de Plantas).

For some Antarctic terrestrial ecosystems, large amounts of organic matter of marine origin were seasonally deposited on ice-free soils by birds and mammals, especially penguins, enhancing biodiversity and complexity. The incorporation of this material into the soil mineral matrix became the main pathway for the widespread formation of phosphate minerals and the so-called ornithogenic soils, comparatively well-studied in the context of Maritime Antarctica. We aimed to study the influence of penguins on soil formation at Hope Bay, a transition climatic zone, where no previous pedological study has been undertaken relation to soil phosphatization. Ten pedons, nine of which ornithogenic, were described and sampled and physical, chemical and mineralogical properties analyzed. Results indicate that the slow mineralization of bird droppings (guano), coupled with high levels of organic matter and reduced bases leaching, notably Ca, contributed to reduce soil acidification and exchangeable Al^{3+} content, unlikely ornithogenic soils in the Maritime Antarctic zone. Phosphate minerals typical of the phosphatization process, such as taranakite, minyulite, leucophosphite, struvite, and fluorapatite, were detected. In Hope Bay, they seem to be immobilized for a long time, by very slow rates of dissolution, neoformation of secondary phosphatic minerals, mineralogical transformation and leaching processes. In this case, ornithogenesis was basically a mechanism of sea-land nutrient transfer, enriching the latter, since the parent rocks are chemically poor sedimentary parent material. On the other hand, the presence of X-ray diffraction

peaks at 0.72 nm and 0.35 nm, characteristic of kaolinite, indicate that climate conditions at Hope Bay were variable, with periods with greater moisture and more favorable for chemical and mineralogical changes in the past, thus the current environment is dominated by the phosphatization process on previously weathered sedimentary material.

RESUMO

PEREIRA, Thiago Torres Costa. **Gênese, mineralogia e significância ecológica de solos ornitogênicos de uma superfície polar semi-desértica em Hope Bay, Península Antártica.** Viçosa: UFV, 2012. Cap. 4 (Tese – Doutorado em Solos e Nutrição de Plantas).

Alguns ecossistemas terrestres da Antártica possuem grande aporte de materiais orgânicos depositados por aves e mamíferos, com destaque para os pinguins, sendo a incorporação destes materiais orgânicos à matriz mineral do solo a principal influência na formação dos minerais de argila fosfatados e na caracterização dos solos ornitogênicos. Desta forma, o objetivo do trabalho foi estudar a influência das aves (pinguins) no processo de enriquecimento dos solos em Hope Bay, bem como discutir questões relacionadas aos aspectos físicos, químicos e mineralógicos destes solos no que se refere à fosfatização dos mesmos. Assim, foram descritos e coletados 10 perfis de solos, 9 dos quais ornitogênicos, submetidos às análises físicas, químicas e mineralógicas. Os resultados indicam que a lenta mineralização do guano, associado aos elevados teores de matéria orgânica e menor lixiviação de bases, principalmente Ca, contribuem para menor acidificação dos solos e menor teor médio de Al^{3+} ($0,58 \text{ cmol}_c \text{ dm}^{-3}$), fato pouco esperado para solos ornitogênicos da Antártica Marítima. Minerais típicos do processo de fosfatização como taranakita, minyulita, leucofosfita, struvita e fluorapatita foram detectados. Em Hope Bay, estes parecem ser imobilizados por mais tempo, pela lenta ação dos processos que envolvem a dissolução, neoformação de minerais secundários fosfáticos, transformação mineralógica e lixiviação. Neste caso, o processo de ornitogênese representa um importante mecanismo de transferência de nutrientes do mar para o continente, com enriquecimento deste último, principalmente por tratar-se de um ambiente cujo material parental é pobre quimicamente. A presença de picos em 0,72 nm e 0,35 nm, bem característicos da caulinita, indicam para Hope Bay um passado mais favorável às alterações químicas e transformações mineralógicas, sendo o ambiente atual submetido ao processo de fosfatização sobre material de natureza sedimentar previamente intemperizado.

1. INTRODUCTION

In the short summer season, the ice-free terrestrial environments of Antarctica, experience a direct influence on the trophic relationships and transfer pathways of mass and energy between the ocean and coastal areas (Rakusa-Suszczewski, 1993). At these locations, large amounts of organic matter are deposited by birds and mammals, especially by penguins. The incorporation of organic matter into the soil mineral matrix strongly influences the formation of clay minerals and secondary phosphate, forming the characteristic "ornithogenic soil" (Tatur and Myrcha, 1989; Tatur, 2002; Schaefer et al., 2004; Simas et al., 2007), a term originally proposed by Syroechkovsky (1959).

The annual deposition of penguin guano reaches 10 kg m^{-2} of excreta, representing the most abundant source of organic matter in Antarctic terrestrial ecosystems (Rakusa-Suszczewski, 1980). However, unlike dry areas from elsewhere where guano is accumulated, most nutrients carried onshore by penguins soon return to the sea as partially mineralized guano in suspension. However, under favorable conditions, more than 10 % of the P in this amount can be incorporated into the soil (Myrcha and Tatur, 1991), indicating that the nutrient concentration and high turnover may be important for the productivity, structure and distribution of naturally nutrient-poor coastal ecosystems, such as those of Hope Bay.

In cold polar desert or semi-desert areas of Antarctica, the deposition of guano apparently has little influence on minerals alteration (Ugolini, 1972). However, under a moderately humid climates of Maritime Antarctica, the intense cryoturbation and water percolation incorporate leachate with depth. These N and phosphorus-rich leachates from these systems reacts with the mineral substrate in a complex process of soil phosphatization, first described by Tatur and Barczuk (1985), and recently detailed by Michel et al. (2006), Simas et al. (2006) and Simas et al. (2007). High amounts of P are found in areas of phosphatized rock, e.g., Ca-phosphate and Fe-Al-phosphate, formed by the action of chemically reactive solutions released by the weathering of primary phosphates (including guano) on rocky substrates.

Secondary phosphate minerals such as taranakite, minyulite and leucophosphite are newly formed by the intense P mobilization, in a peculiar process

of phosphatization in a cryogenic environment (Tatur, 2002, Schaefer et al., 2008). In addition, other rare phosphate clay minerals, unlikely to occur in soils of other natural terrestrial environments can be observed (Tatur and Myrcha, 1989, Tatur, 2002), being also found on Brazilian oceanic islands, similarly developed from bird guano (Oliveira et al., 2010, Schaefer et al., 2010).

Ornithogenic are clearly distinguished from non-ornithogenic soils by several properties, e.g., low pH and base saturation, very high P (Mehlich-1), exchangeable Al and normally total organic carbon (TOC) levels (Simas et al., 2007). On some of these soils, oases with extensive and continuous vegetation cover are formed, where the microbial activity is higher than usual in Antarctic soils (Tatur et al., 1997, Michel et al., 2006).

The purpose of this study was to assess the influence of birds (penguins) on the process of soil enrichment in Hope Bay, as well as to discuss issues related to physical, chemical and mineralogical properties of soils with regard to their phosphatization, in a context of a transitional peninsular climate between the wetter Maritime Antarctica and the dry, cold deserts of the Weddell Sea sector.

2. MATERIAL AND METHODS

2.1. Study area

The study was conducted in Hope Bay, in the northern end of the Antarctic Peninsula. The study area is bordered in the South by Mount Flora (520 m asl) and in the East by the Buenos Aires glacier, whose snout reaches over 100 m. Scar (2002) defined the area of Mount Flora and surroundings as an Antarctic Specially Protected Area (ASPA 148). Excluding Mount Flora, the ice-free area between the sea and the glaciers covers a region of approximately 3 km², with average elevations of ≤ 100 m (Birkenmajer, 1993a, Martin-Serrano et al., 2005).

According to Köppen's classification, the region is part of the EF (polar) climate. The average temperature of Hope Bay measured at Esperanza Station, between 1952 and 2010 was -5.1 °C, with annual precipitation of approximately 150 mm, characterizing a semi-desert climate.

The geology of Hope Bay is composed of a metasedimentary (Trinity Peninsula Group - Hope Bay Formation: marine siliciclastic turbidites and sandstones), sedimentary (Botany Bay Group - Mount Flora Formation: sandstones, conglomerates and schists) and volcanic rock sequences (Antarctic Peninsula Volcanic Group - Kenney Glacier Formation: rhyolite-dacites, ignimbrites, conglomerates and cemented tuff) (Birkenmajer 1993b; del Valle et al. 2001; Scar, 2002).

The geomorphology is related to both paraglacial and periglacial processes and landforms, reflecting the widespread late Quaternary retreat of glaciers (Martín-Serrano et al., 2005), with shorter intervals of minor glacial advances. Most geomorphic processes are related to the coastal environmental, with persistent winds, summer melting, and increasing periglacial erosion, specially thermokarst features.

2.2. Soil sampling

Ten pedons were described and sampled based on criteria established by Antarctic Permafrost and Soils (ANTPAS, 2006). Of these, nine pedons were

recognized and classified as "ornithogenic". Pedon HB19, a representative non-ornithogenic soil was used as a reference for comparison with the others. Soils were classified according with USDA Soil Taxonomy (Soil Survey Staff, 2010), with some adaptations.

2.3. Physical, chemical and mineralogical analysis

The granulometry of soils was determined, with adaptations for clay dispersion (Ruiz, 2005). Soil pH was determined in distilled water and 1 mol L⁻¹ KCl solution; total organic carbon (TOC) and the carbon content for each fraction were quantified in extracts from the fulvic acid, humic acid and humin fractions (Yeomans and Bremner, 1988); available P, Na⁺ and K⁺ exchangeable were determined after extraction with 0.5 mol L⁻¹ HCl + 0.0125 mol L⁻¹ H₂SO₄ (Mehlich-1); Ca²⁺, Mg²⁺ and Al³⁺ by titration after extraction with 1 mol L⁻¹ KCl; potential acidity (H + Al) by titration after extraction with 0.5 mol L⁻¹ Ca(CH₃COO)₂ at pH 7.0; CaCO₃ by titration after extraction with 0.5 mol L⁻¹ HCl. All chemical analyses complied with SSSA (1996) and Embrapa (1997).

The total digestion of the ground and sieved (0.25 mm) fine earth (< 2 mm) was carried out by a HCl, HNO₃ and HF digestion, performed in a microwave oven (CEM/MDS 2000) according to the EPA method 3052 (USEPA, 2011). The total amounts of Ca, Mg, K, Fe, Al, Mn, and P were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES).

The minerals in the total air-dried soil were identified by X-ray diffraction (XRD). For the clay fraction, the following treatments were performed: Fe-removal by dithionite-citrate-bicarbonate (DCB) (Mehra and Jackson, 1960); saturation with 1.0 mol L⁻¹ KCl; heating in an oven at 350 °C and 550 °C for 3 hours each; saturation with 1.0 mol L⁻¹ MgCl and glycerol solvation. A diffractometer (PANalytical / X'Pert Pro) was used, with CoK α radiation in the range between 4 and 50 °2 θ , at intervals from 0.017 °2 θ to 1 step s⁻¹, at a voltage of 40 kV and current of 30 mA. The interpretation of XRD data was based on Bish and Post (1989).

The fine earth (< 2 mm) was ground and sieved (0.25 mm) for extractions with: citrate-bicarbonate-dithionite (three successive extractions) (Mehra and Jackson, 1960), and ammonium acid oxalate at pH 3.0 (McKeague and Day, 1966). After both extractions, Fe, Al and P amounts were determined by ICP-OES.

3. RESULTS AND DISCUSSION

3.1. General characterization of the studied area

Table 1 illustrates the general features of each soilscape. All soils colonized by penguins (*Pygoscelis adeliae*), phosphates were detected, sometimes preserved well into the permafrost substrate, indicating warmer past conditions, in which P-rich leachates reached lower depths, and permafrost was absent, or active layer was deeper.

These ornithogenic soils are clearly differentiated from the non-ornithogenic reference pedon (HB19) with regard to the presence of vegetation. However, even "ornithogenic" areas show a limited vegetation usually sparse and poor, composed mainly of crustose lichens, green algae (*Prasiola crispa*), with very little moss cover, restricted to poorly drained areas under higher moisture regime. The absence of higher plant species (*Deschampsia antarctica* and *Colobanthus quitensis*) in Hope Bay is noticeable, unlike their common occurrence on ornithogenic soils on the South Shetland Islands (Tatur, 2002, Schaefer et al., 2004, Michel et al., 2006, Simas et al., 2006, Simas et al., 2007, Simas et al., 2008).

This fact is related to a much drier colder climate condition in Hope Bay, located in a transition zone to the so-called "polar desert" of the Weddell Sea sector (Bockheim and Ugolini, 1990, Blume et al., 1997). Thus, lower temperatures and less liquid water in the summer are decisive factors for establishment of diverse or abundant plant communities.

Table 1. Description, classification and location of selected pedons

Pedon	Alt. (m.s.l.) ¹	Vegetation ²	SC ³	Description	GC ⁴
HB1	50	L>P	Ornithogenic Haploturbel	Very rocky, cryoturbated and phosphatized soil; terrain from flat to gently undulating, with active erosion and solifluction, controlled by the drainage incision caused by widespread thermokarst	499991 2669558
HB2	44	L	Ornithogenic Haploturbel	Very rocky, cryoturbated and phosphatized soil; terrain from flat to gently undulating, with slight erosion and solifluction, controlled by the drainage incision caused by widespread thermokarst	500037 2969642
HB4	117	L>P	Ornithogenic Haploturbel	Very rocky, cryoturbated soil with evolved phosphatization, mineralized between pebbles; terrain gently undulating, with active erosion and solifluction	499578 2969027
HB5	45	Absent	Ornithogenic Haplohemist	Sediment of lacustrine algae (chlorophytes + cyanobacteria), phosphatic; receives melt-water in channels from the central penguin rookery descending towards lake Boeckella; flat terrain	499892 2969235
HB7	50	L>P	Ornithogenic Haploturbel	Very rocky, cryoturbated soil with evolved phosphatization and mineralized between pebbles; terrain gently undulating, with slight erosion and solifluction	499560 2969687
HB10	52	Absent	Ornithogenic Haploturbel	Soil under current penguin colony; very rocky, cryoturbated and phosphatized; terrain gently undulating, with slight erosion and solifluction	499565 2969659
HB11	8	L>P	Ornithogenic Gelorthent	Very rocky, cryoturbated and phosphatized soil with fragipan under periglacial cover, with phosphates cemented in deeper layers; uplifted marine terrace, with several types of gravel; terrain gently undulating	500528 2969918
HB16	12	P	Ornithogenic Gelorthent	Rocky, cryoturbated and phosphatized soil, on an uplifted marine terrace, with various kinds of gravel; relief flat, with erosion in the form of solifluction	499996 2970276
HB17	46	P	Ornithogenic Haploturbel	Very rocky, cryoturbated and phosphatized soil. Large amounts of penguin bones at the site. Relief flat, with slight erosion and solifluction controlled by the drainage incision caused by widespread thermokarst	500013 2969451
HB19	144	Absent	Lithic Haploturbel	Very rocky and cryoturbated soil; mountainous terrain, with moderate to severe erosion	499994 2968639

¹ meters above sea level; ² L – lichens, P – *Prasiola crispa*; ³ soil classification, adapted from Soil Survey Staff (2010); ⁴ geographic coordinate, zone 21S datum WGS 84.

In the ornithogenic soils constraining, without a more plant cover, or on lake fringes (HB5), active penguin trampling and toxicity of fresh guano during the nesting period limit or prevent plant growth.

Crustose lichens occasionally occur in soilscape HB19, and can be disregarded. In this case, the factors that appear to control the establishment of vegetation are the absence of fertilization by birds (see chemical properties), associated with a greater exposure to strong winds and higher altitude, with near-surface permafrost year round.

3.2. Soil morphology and physical properties

The structural development of the soils was moderate to weak, varying mainly between subangular blocky and granular (Table 2). According to Bockheim and Tarnocai (1998), the blocky or granular structures at the surface and solid-looking subsurface materials are gelic material typical of cryopedogenesis.

In the ornithogenic soils of Hope Bay the transition from surface to subsurface horizons is usually clear, with a usually dark to grayish surface horizon, with higher organic matter, and bleached phosphatic B and/or C horizon, down the pedon. In the non-ornithogenic soil, the differentiation between horizons is less clear, due to the lack of organic input, with much vegetation cover even absence.

All soils vary from gravelly to very gravelly, with a relatively high proportion of clay in ornithogenic soils, a feature that can also be attributed to a warmer period in the past, when neoformation of secondary phosphate minerals reached lower depths. Areas of current penguin colonies and surroundings (HB7 and HB10) are those in which phosphate most contributes to the increasing clay. On non-ornithogenic soil, the absence of phosphatization accounts for much lower clay content, about 2.5 dag kg⁻¹ (Table 2).

Cryoturbation occurs in all soils, by the wavy/broken transitions between soil horizons, as well as for the erratic distribution of clay, silt and pebbles along the pedon (Table 2). According to Bockheim and Tarnocai (1998), poor drainage, higher silt contents, frequent freeze-thaw cycles, and permafrost to a depth of 1 m in the pedon are conditions that favor cryoturbation (cryopedogenesis). In this case, cryoturbic features may be inherited from past deeper active layer under warmer/wetter condition.

Table 2. Some morphological and physical properties of the studied soils

Ped.	Depth (cm)	Structure ¹	Transition	Color (dry)	Skel. ²	Sand	Silt	Clay
					-----dag kg ⁻¹ -----			
HB1 - Ornithogenic Haploturbel								
A1	0-8	w m bl/md m gr	clear wavy	7.5YR 4/2	65	62	21	17
B2	30-45/50	w m gr	clear flat	10YR 5/4	47	53	27	20
C	90-130+	w m gr/ma	diffuse irregular	2.5Y 6/2	54	91	6	3
HB2 - Ornithogenic Haploturbel								
A	0-15/25	md m bl/md m gr	clear wavy	10YR 5/2	52	61	24	15
B2	30/40-55	st m gr	gradual wavy	5Y 6/1	35	70	23	7
C2	160-210	md m bl	-	5Y 6/1	41	50	30	20
HB4 - Ornithogenic Haploturbel								
A	0-10	st m gr	gradual wavy	10YR 5/3	48	44	38	18
B	20-40	st m gr	gradual irregular	10YR 5/4	71	51	31	18
HB5 - Ornithogenic Haplohemist								
O	0-30	st m cr	-	5Y 3/2	0	11	58	31
HB7 - Ornithogenic Haploturbel								
A	0-10	md m gr	clear wavy	7.5YR 3/3	74	55	13	32
B1	10-30	st m gr	gradual irregular	10YR 5/4	67	55	16	29
B3	50-70	md m bl/md m gr	gradual irregular	2.5Y 7/3	67	52	25	23
HB10 - Ornithogenic Haploturbel								
A	0-10	w m bl	gradual wavy	10YR 6/3	60	24	37	39
B2	45-90	w m bl/w m gr	gradual wavy	2.5Y 7/3	55	27	32	41
HB11 - Ornithogenic Gelorthent								
A	0-10	w m bl/sg	clear wavy	2.5Y 6/2	58	88	7	5
3Ax	35-60	md m gr/sg	clear wavy	2.5Y 6/3	62	94	3	3
3Cx	60-85	md m gr/sg	clear wavy	2.5Y 6/4	26	97	1	2
4A	85-120	sg	clear flat	2.5Y 6/2	73	94	4	2
HB16 - Ornithogenic Gelorthent								
A	0-10	sg	clear wavy	10YR 6/3	52	81	9	10
C2	29-50	sg	-	2.5Y 7/2	40	91	3	6
HB17 - Ornithogenic Haploturbel								
A	0-10	-	abrupt flat	5Y 5/3	25	33	47	20
AB	10-15	-	-	5Y 5/1	40	35	44	21
2A	35-43	-	-	5Y 6/2	39	68	20	12
3A	60-72	-	-	5Y 6/2.5	33	49	28	23
HB19 - Lithic Haploturbel								
A	0-10	md m gr	diffuse irregular	-	27	52	45	3
C	30-60	w m bl/w m gr	-	-	36	53	45	2

¹ Development: w = weak, md = moderate, st = strong. Size: m = medium. Type: ma = massive, gr = granular, bl = subangular blocky, sg = single grain, cr = crumbs; ² Percent of particles > 2 mm.

3.3. Chemical properties

The ornithogenic soils are mostly dystrophic (Table 3). This finding is in agreement with Schaefer et al. (2004), Michel et al. (2006) and Simas et al. (2008), for ornithogenic soils from the South Shetlands archipelago. Even with high bases sum (approximately 15.00 cmol_c dm⁻³ for the pedons HB1 and HB4), the soils were dystrophic due to the higher potential acidity, possibly influenced by high organic matter enhancing acidity.

Table 3. Chemical properties of the studied soils

Ped.	Depth (cm)	pH		Ca ²⁺	Mg ²⁺	K ⁺	Na ⁺	Al ³⁺	H+Al	BS	CEC	PBS	m ¹ -----%	Na ²	P mg dm ⁻³
		H ₂ O	KCl												
HB1 - Ornithogenic Haploturbel															
A1	0-8	4.66	4.29	10.46	4.77	0.38	1.03	0.67	19.50	16.64	36.14	46.00	3.90	5.94	8675.80
B2	30-45/50	4.42	3.87	10.35	1.68	0.73	1.37	1.33	20.60	14.13	34.73	40.70	8.60	8.89	8059.80
C	90-130+	4.89	3.64	6.32	0.59	1.82	0.45	0.57	20.70	9.18	29.88	30.70	5.80	4.60	1296.10
HB2 - Ornithogenic Haploturbel															
A	0-15/25	4.15	3.42	3.29	0.79	0.27	0.94	0.86	23.30	5.29	28.59	18.50	14.00	15.32	4437.20
B2	30/40-55	4.37	3.29	2.19	0.47	0.35	0.40	2.29	17.90	3.41	21.31	16.00	40.20	6.96	1606.20
C2	160-210	6.95	6.23	3.49	1.41	0.48	0.12	0.00	0.80	5.50	6.30	87.30	0.00	2.10	353.40
HB4 - Ornithogenic Haploturbel															
A	0-10	5.25	4.89	10.00	2.23	0.21	1.68	0.29	23.30	14.12	37.42	37.70	2.00	11.63	7570.30
B	20-40	4.42	3.86	10.41	3.39	0.66	1.76	0.67	22.50	16.22	38.72	41.90	4.00	10.44	6728.80
HB5 - Ornithogenic Haplohemist															
O	0-30	4.96	4.50	5.20	1.12	0.20	0.47	0.10	9.10	6.99	16.09	43.40	1.40	6.57	2952.70
HB7 - Ornithogenic Haploturbel															
A	0-10	5.52	4.40	2.63	1.26	0.31	1.20	0.48	9.10	5.40	14.50	37.20	8.20	20.43	7778.10
B1	10-30	4.50	3.52	2.23	1.01	0.30	1.20	0.86	19.00	4.74	23.74	20.00	15.40	21.45	7572.40
B3	50-70	4.56	3.55	7.33	0.62	0.45	1.68	0.86	17.80	10.08	27.88	36.20	7.90	15.32	6361.30
HB10 - Ornithogenic Haploturbel															
A	0-10	6.72	6.31	1.45	4.56	2.91	5.52	0.00	20.70	14.44	35.14	41.10	0.00	35.01	8326.50
B2	45-90	5.43	3.75	4.50	3.77	2.41	2.19	1.05	14.80	12.87	27.67	46.50	7.50	15.77	9314.60
HB11 - Ornithogenic Gelorthent															
A	0-10	4.80	3.37	1.73	0.66	0.53	0.88	0.86	9.10	3.80	12.90	29.50	18.50	18.80	920.10
3Ax	35-60	4.89	3.24	0.54	0.36	1.27	0.79	0.86	7.20	2.96	10.16	29.10	22.50	20.78	395.70
3Cx	60-85	4.91	3.16	1.10	0.39	1.29	0.66	0.86	8.80	3.44	12.24	28.10	20.00	15.35	630.30
4A	85-120	4.85	3.38	1.10	0.48	1.16	0.85	1.33	7.50	3.59	11.09	32.40	27.00	17.36	1683.80
HB16 - Ornithogenic Gelorthent															
A	0-10	6.59	5.28	2.92	2.01	0.89	5.31	0.00	6.30	11.13	17.43	63.90	0.00	47.71	4958.80
C2	29-50	5.74	4.42	1.97	1.86	0.43	2.77	0.00	5.50	7.03	12.53	56.10	0.00	37.89	6571.80
HB17 - Ornithogenic Haploturbel															
A	0-10	7.28	6.65	1.51	12.43	0.73	1.55	0.00	10.70	16.22	26.92	60.30	0.00	9.55	10449.30
AB	10-15	6.46	5.92	1.45	8.37	0.75	0.71	0.00	5.70	11.28	16.98	66.40	0.00	6.20	4288.70
2A	35-43	7.18	6.59	0.85	7.64	0.76	0.21	0.00	4.40	9.46	13.86	68.30	0.00	2.24	1843.80
3A	60-72	6.93	6.33	2.47	6.77	0.89	0.20	0.00	2.80	10.33	13.13	78.70	0.00	1.97	860.20
HB19 - Lithic Haploturbel															
A	0-10	7.07	5.81	3.61	1.13	0.20	0.29	0.00	0.30	5.23	5.53	94.60	0.00	5.47	97.50
C	30-60	7.02	6.00	3.64	1.20	0.21	0.24	0.00	0.50	5.29	5.79	91.40	0.00	4.50	170.60

¹Al saturation; ²Na saturation.

The mean values of bases sum ($9.09 \text{ cmol}_c \text{ dm}^{-3}$ in the ornithogenic soils and of $5.26 \text{ cmol}_c \text{ dm}^{-3}$ found in the non-ornithogenic pedon HB19) indicate the contribution of ornithogenesis for increasing nutrients contents.

The pH values, although low in some pedons, e.g., in HB2 (Table 3), are similar to ornithogenic soils from elsewhere in the Maritime Antarctic, with an average 5.43; this is higher than reported by Schaefer et al. (2004), Michel et al. (2006) and Simas et al. (2007). Guano is initially alkaline, but progressive acidification occur with advancing microbial organic matter degradation. The slow degradation of organic compounds and longer preservation of guano, evident in Hope Bay, since guano was still fresh even at the end of summer, e.g., in HB10, accounting for mean pH values of 6.08 in this pedon. This lower microbial activity is possibly determined by lower average temperatures in Hope Bay compared with the South Shetland Islands.

The reduced leaching of bases in Hope Bay, due to the lower amount of liquid water in the summer, possibly resulted in a more efficient buffering effect against soil acidification. These effects also seem to have influenced the results of exchangeable Al^{3+} , which were lower than reported by Schaefer et al. (2004), Michel et al. (2006) and Simas et al. (2007), in highly developed and more acidic ornithogenic soils. This finding contradicts the idea that ornithogenic soils should necessarily have high levels of exchangeable Al^{3+} .

The Mehlich-1 extractable P levels in the ornithogenic soils were very high (average $4,734 \text{ mg dm}^{-3}$), reaching $10,449 \text{ mg dm}^{-3}$ in the A horizon of pedon HB17 (Table 3). Mehlich-1 is commonly used for extraction from soils with low P values, especially in more oxidized soils of acid environments. In the extremely acid reaction during extraction procedure ($\text{pH} < 2.0$), it is possible to overestimate, given the fact that in P-rich soils, this extractor can solubilize primary, stable Ca-P forms (Novais and Smyth, 1999), although high P results were expected.

All ornithogenic soils of Hope Bay were classified as "strongly ornithogenic" according to the criteria proposed by Simas et al. (2007). This reflects the great and widespread influence of penguins on the enrichment of soils in Hope Bay, naturally developed from chemically poor sedimentary substrates. Summing up, such soils colonized by birds for long periods of time, and rich in P, can be considered as the most representative products of phosphatization (Tatur, 1989; Myrcha and Tatur, 1993, Blume et al., 2002, Schaefer et al., 2004, Simas et al., 2006).

3.4. Total organic carbon and humic substances

The average amount of soil organic carbon was 5.94 dag kg⁻¹, reaching a maximum of 21.72 dag kg⁻¹ in the HB7 pedon (Table 4).

Table 4. Quantitative fractioning of the organic matter of the studied soils

Pedon	Depth (cm)	TOC	FA	HA	HU	HA	HI ¹
						FA	%
-----dag kg ⁻¹ -----							
HB1 - Ornithogenic Haploturbel							
A1	0 - 8	13.44	1.72	7.70	2.27	4.48	87
B2	30 - 45/50	9.62	1.19	6.07	1.21	5.10	88
C	90 - 130+	1.75	0.30	1.02	0.19	3.40	86
HB2 - Ornithogenic Haploturbel							
A	0 - 15/25	6.24	2.19	1.44	1.81	0.66	87
B2	30/40 - 55	2.17	0.95	0.17	0.72	0.18	84
C2	160 - 210	0.99	0.42	0.12	0.25	0.29	80
HB4 - Ornithogenic Haploturbel							
A	0 - 10	11.05	2.94	1.94	5.53	0.66	94
B	20 - 40	10.16	2.44	2.69	4.33	1.10	93
HB5 - Ornithogenic Haplohemist							
O	0-30	9.28	1.93	2.43	4.10	1.26	91
HB7 - Ornithogenic Haploturbel							
A	0 - 10	21.72	5.15	9.42	4.74	1.83	89
B2	30 - 50	13.86	1.73	7.14	3.79	4.13	91
B3	50 - 70	3.90	1.24	1.44	0.78	1.16	89
HB10 - Ornithogenic Haploturbel							
A	0 - 10	8.53	1.19	2.94	3.67	2.47	91
B2	45 - 90	6.44	1.64	1.60	2.53	0.98	90
HB11 - Ornithogenic Gelorthent							
A	0 - 10	1.23	0.74	0.14	0.21	0.19	89
3Ax	35 - 60	0.90	0.51	0.09	0.14	0.18	83
3Cx	60 - 85	0.74	0.43	0.05	0.17	0.12	88
4A	85 - 120	0.71	0.40	0.05	0.13	0.13	82
HB16 - Ornithogenic Gelorthent							
A	0 - 10	3.85	0.67	1.21	1.68	1.81	92
C2	29 - 50	1.55	0.63	0.19	0.61	0.30	92
HB17 - Ornithogenic Haploturbel							
A	0 - 10	8.70	0.95	1.05	5.00	1.11	80
AB	10 - 15	3.77	0.55	0.45	2.23	0.82	85
2A	35 - 43	1.12	0.20	0.17	0.58	0.85	85
3A	60 - 72	0.92	0.18	0.17	0.47	0.94	88
HB19 - Lithic Haploturbel							
A	0 - 10	1.50	0.15	0.30	0.85	2.00	86
C	30 - 60	0.93	0.09	0.13	0.53	1.44	80

¹ Humification index = (FA/TOC + HA/TOC + HU/TOC)

These values exceed those reported by Simas et al. (2007) for similar soils from the Maritime Antarctica, indicating greater accumulation and, possibly,

increased condensation of organic compounds in the cooler, drier (Hope Bay) area. In the non-ornithogenic pedon HB19, the levels of organic carbon were lower (on average 1.22 dag kg^{-1}). The marked importance of penguins for increasing organic compounds in Antarctic terrestrial ecosystems is highlighted by values for reference soils (HB19) in a similar trend with South Shetland archipelago ornithogenic soils.

The mineral fraction of soils plays a major role on the quantity and quality of organic matter in soils, which partly depends on the adsorption on clay surfaces (Oades, 1988) for organic matter stabilization. In addition, other factors influence the stabilization and preservation of organic matter in soils, e.g., the extremely low temperatures in Antarctica (Michel et al., 2006), so that low temperatures and moisture, are crucial for the low microbial activity and humification rate (formation of humic substances) of Antarctic soils.

Michel et al. (2006) indicated another factor for the preservation of these organic compounds – the amorphous nature of the mineral fraction, with adsorption capacity helping to protect against the microbial degradation. The high ratios of Fe_o/Fe_d and Al_o/Al_d (see mineralogy) indicate the predominance of less crystalline mineral forms in soil, which may be another important factor in the preservation of organic matter in the ornithogenic soils of Hope Bay.

Among the existing humification pathways (degradative pathway and polymerization pathways), Silva and Mendonça (2007) showed that in very cold areas, where microbial limited activity prevails, the degradation of recalcitrant biopolymers (lignin, cutin, suberin, melanin) and the eventual formation of humin (HU), humic acids (HA) and fulvic (FA) is predominant. However, very little lignin is present in these soils, if any at all. Thus, the seemingly abrupt reduction of organic carbon in the depth of almost all pedons, according to Simas et al. (2007), is related to the absence of higher plants (*D. Antarctica* and *C. quitensis*), which are responsible for the incorporation of lignin from the root system into the soil.

Consequently, the humic substances in these environments where lignin does not occur have been necessarily formed by the condensation of amino sugar compounds, or by reactions between ketones and amino acids (Michel et al., 2006). Regardless of the predominant pathway, humification is a process in which the C previously in more labile forms is progressively stabilized, contributing to soil C fixation (Silva and Mendonça, 2007), even in dry, cold polar desert soils.

The fractionation of humic substances in ornithogenic soil indicated, on average, 1.26 dag kg⁻¹ fulvic acids (FA), 2.07 dag kg⁻¹ humic acids (HA), and 1.96 dag kg⁻¹ humin (HU) (Table 4). According to Zech et al. (1997), the increased humification process enriches the humic substances in condensed, recalcitrant and aromatic structures, resulting in higher proportion HA fraction. The ratio HA/FA found in soils of Hope Bay (on average 1.64) indicates a higher degree of humification, which agrees with the mean result of 88 % of the calculated humification index.

The pattern of increasing HA/FA ratio with depth, as observed by Michel et al. (2006), explained the migration and reaction of organic matter along the pedon, causing polycondensation and accumulation of the more recalcitrant humic substances. This pattern was not observed in the soils of Hope Bay, probably due to the higher cryoturbation and greater movement of humic substances in the upper horizons (A and B), and the presence of permafrost closer to the surface.

3.5. Total elemental composition

The total contents of CaO, MgO and K₂O were, on average, 3.92 dag kg⁻¹, 0.66 dag kg⁻¹ and 2.42 dag kg⁻¹ for ornithogenic soils, and 1.63 dag kg⁻¹, 0.52 dag kg⁻¹ and 2.64 dag kg⁻¹ for the non-ornithogenic pedon, respectively (Table 5).

Similar results were found by Tatur (1989) for penguin rookeries surface samples in the same area. There was a consistent results between the aqua regia digestion used by Tatur (1989) and the triacid attack (HCl + HNO₃ + HF) used in the present study, especially for MgO and K₂O.

Table 5. Total results for < 2 mm air-dried soil samples

Pedon	Depth (cm)	CaO	MgO	K ₂ O	Fe ₂ O ₃	Al ₂ O ₃	MnO	P ₂ O ₅
-----dag kg ⁻¹ -----								
HB1 - Ornithogenic Haploturbel								
A1	0 - 8	8.22	0.88	2.00	1.92	9.22	0.01	10.84
B2	30 - 45/50	9.10	0.81	1.88	2.61	9.20	0.05	13.42
C	90 - 130+	1.70	0.52	3.33	4.62	5.04	0.03	5.91
HB2 - Ornithogenic Haploturbel								
A	0 - 15/25	2.11	0.54	2.53	3.45	4.90	0.03	4.62
B2	30/40 - 55	1.89	0.58	3.01	3.82	5.50	0.03	1.96
C2	160 - 210	1.84	0.63	2.95	5.02	4.89	0.07	0.21
HB4 - Ornithogenic Haploturbel								
A	0 - 10	11.04	0.88	1.28	0.87	1.45	0.07	22.48
B	20 - 40	2.53	0.68	2.76	5.58	1.22	0.02	10.56
HB5 - Ornithogenic Haplohemist								
O	0-30	2.17	0.63	2.38	3.55	1.61	0.03	3.09
HB7 - Ornithogenic Haploturbel								
A	0 - 10	2.22	0.68	1.78	2.78	3.23	0.01	2.29
B2	30 - 50	2.59	0.62	2.34	5.53	3.62	0.01	6.41
B3	50 - 70	12.63	0.68	2.68	5.28	4.47	1.10	8.31
HB10 - Ornithogenic Haploturbel								
A	0 - 10	5.86	0.92	2.43	0.80	2.72	0.02	23.41
B2	45 - 90	5.91	0.72	2.62	3.20	3.18	0.02	19.79
HB11 - Ornithogenic Gelorthent								
A	0 - 10	1.79	0.57	2.76	3.43	4.36	0.02	2.26
3Ax	35 - 60	2.04	0.62	2.42	3.30	4.35	0.03	1.32
3Cx	60 - 85	1.88	0.59	2.62	2.83	4.64	0.02	2.23
4A	85 - 120	2.16	0.65	2.49	2.94	4.35	0.03	0.95
HB16 - Ornithogenic Gelorthent								
A	0 - 10	0.65	0.05	2.23	5.10	3.33	0.04	5.17
C2	29 - 50	1.82	0.55	2.26	3.44	3.38	0.05	4.04
HB17 - Ornithogenic Haploturbel								
A	0 - 10	8.23	1.34	1.43	1.42	1.26	0.11	20.82
AB	10 - 15	2.15	0.63	2.44	4.16	4.17	0.06	2.38
2A	35 - 43	1.72	0.58	2.70	4.10	4.69	0.05	0.69
3A	60 - 72	1.76	0.59	2.74	4.59	4.32	0.06	0.62
HB19 - Lithic Haploturbel								
A	0 - 10	1.68	0.53	2.55	3.81	3.47	0.04	0.10
C	30 - 60	1.58	0.50	2.72	3.59	1.72	0.03	0.11

Higher levels of CaO may be related to reduced leaching of this element, favorable for the formation of phosphatic clays (Tatur, 1989), suggesting the high significant correlation between CaO and P₂O₅ (Table 6). Moreover, plagioclases were detected in all soils (see mineralogy). In this case, the presence of easily weathered primary minerals in the clay fraction indicates a limited chemical weathering and the effect of cryoclasty decreasing the particle size, as suggested by Simas et al. (2006).

Table 6. Correlation matrix of ornithogenic pedons studied

	CaO	MgO	K ₂ O	Fe ₂ O ₃	Al ₂ O ₃	P ₂ O ₅	CaCO ₃	P	TOC
CaO	–	0.64*	-0.53*	-0.44*	0.15	0.73*	0.49*	0.65*	0.37
MgO	–	–	-0.52*	-0.64*	-0.05	0.66*	0.61*	0.56*	0.41*
K ₂ O	–	–	–	0.64*	0.12	-0.53*	-0.70*	-0.66*	-0.62*
Fe ₂ O ₃	–	–	–	–	-0.01	-0.58*	-0.54*	-0.38	-0.29
Al ₂ O ₃	–	–	–	–	–	-0.17	-0.30	-0.05	-0.04
P ₂ O ₅	–	–	–	–	–	–	0.64*	0.80*	0.45*
CaCO ₃	–	–	–	–	–	–	–	0.64*	0.61*
P	–	–	–	–	–	–	–	–	0.74*
TOC	–	–	–	–	–	–	–	–	–

* Significant at 5 %.

The high CaO contents also appear to be associated with the precipitation of CaCO₃, especially in the pedons with higher pH.

The higher total amount of K₂O compared with exchangeable amounts suggests that is present mostly in non-exchangeable forms, possibly associated with the formation of phosphate clays typical of the phosphatization process, as well as associated with the micaceous minerals and K-feldspar in the soil (see mineralogy). However, the negative correlation between K₂O with P₂O₅ (Table 6) suggests that the presence of K in the soil is more related to K-bearing primary minerals. With regard to MgO, lower total levels and relatively higher proportion of exchangeable Mg²⁺ suggests a greater inputs of this element by penguins.

The P₂O₅ results were, on average, 7.24 dag kg⁻¹, reaching 23.41 dag kg⁻¹ in the HB10 pedon (Table 5). In comparison, the non-ornithogenic pedon HB19 showed a P₂O₅ content of 0.11 dag kg⁻¹, which confirms high P enrichment at present or past ornithogenic sites.

The average total contents of Fe₂O₃ and Al₂O₃ of 3.51 and 4.13 dag kg⁻¹, respectively, for the ornithogenic soils, and 3.70 and 2.60 dag kg⁻¹, respectively, in the non-ornithogenic pedon, reveal that these oxides are closely related to the parent material. However, the total Al₂O₃ content at ornithogenic sites was a little higher than in pedon HB19, indicating an increased precipitation of Al-phosphate clays than of Fe-phosphate.

3.6. Mineralogical properties

The X-ray diffraction patterns confirm the presence of a clays mineral assemblage typical of the phosphatization process: taranakite ($\text{K}_3\text{Al}_5(\text{HPO}_4)_6(\text{PO}_4)_2 \cdot 18(\text{H}_2\text{O})$), minyulite ($\text{KAl}_2(\text{PO}_4)_2(\text{OH},\text{F}) \cdot 4(\text{H}_2\text{O})$), leucophosphite ($\text{KFe}_2(\text{PO}_4)_2(\text{OH}) \cdot 2(\text{H}_2\text{O})$), struvite ($(\text{NH}_4)\text{MgPO}_4 \cdot 6(\text{H}_2\text{O})$) and fluorapatite ($\text{Ca}_5(\text{PO}_4)\text{F}$) (Fig. 1). According to Barczuk and Tatur (2003), these minerals are the result of very reactive and supersaturated percolating guano.

At the ornithogenic sites of Hope Bay, these minerals are predominant because the long term inputs of P low bases leaching, especially Ca and K, creating conditions for phosphatization, as discussed by Schaefer et al. (2004), Simas et al. (2007) and Schaefer et al. (2008) for ornithogenic soils on the South Shetland Islands.

In the upper section of phosphatized zones, initially neutral or moderately acidic reactions of guano lead to the formation of struvite, fluorapatite and leucophosphite, of which the latter is the most common. With progressive acidification, minyulite is formed, and as pH lowers even more, there is a tendency to the formation of taranakite.

Taranakite is a secondary phosphate mineral originated in Al-rich environments, also called a potassium aluminum-phosphate (Roberts et al., 1974). However, the comparable amounts of total Fe_2O_3 to total Al_2O_3 indicate a possible substitution of Al by Fe in this mineral structure. Studies by Oliveira et al. (2010) on taranakites on Brazilian oceanic islands point to the occurrence of "ferric taranakite" (or some other unknown phosphate) in view of the high Fe_2O_3 levels in the mineral. Obviously, the term "ferric" does not apply to this study, in spite of the possibility of raising the question of isomorphic replacements in the studied minerals of Hope Bay.

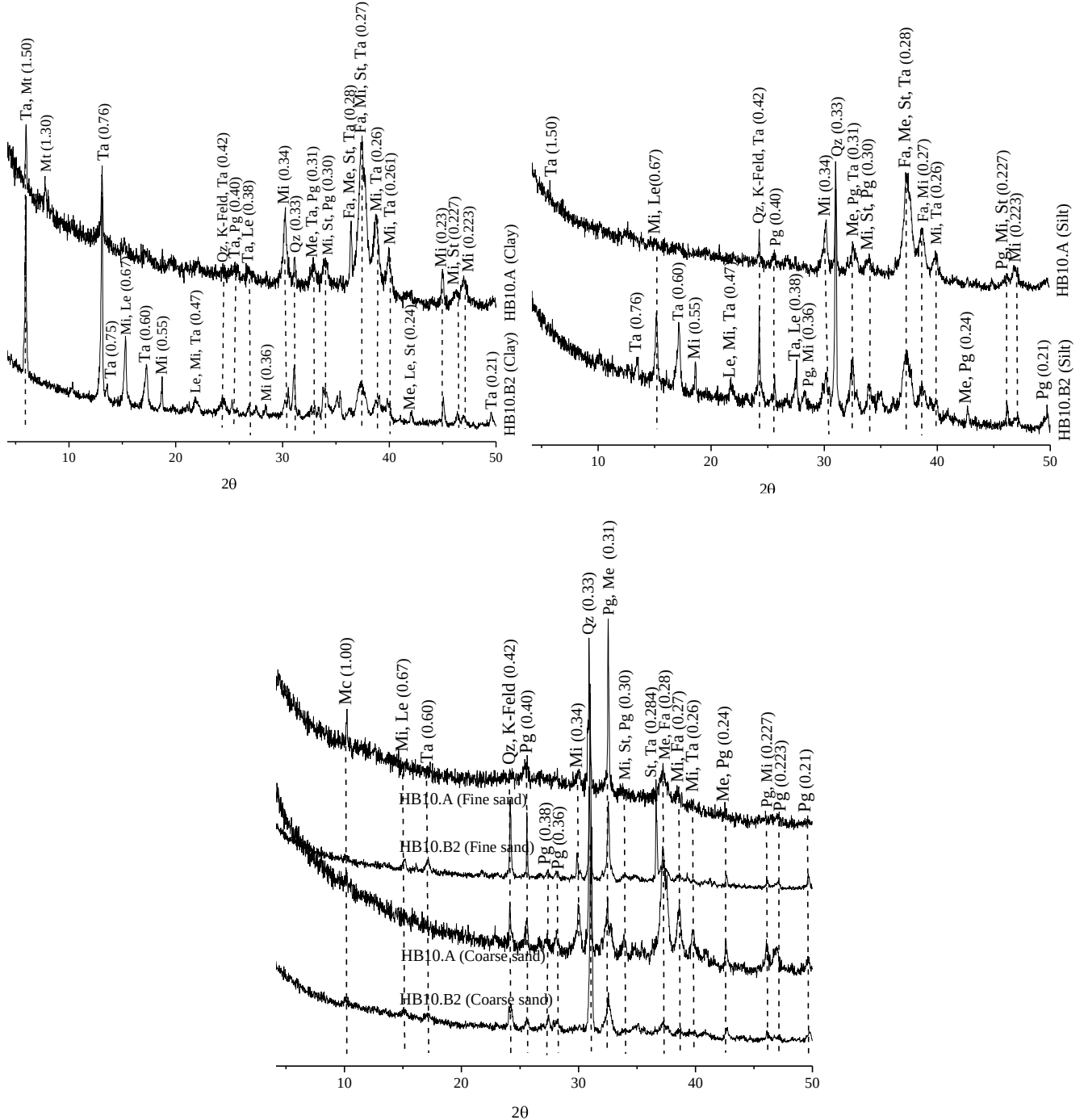


Fig. 1. XRD patterns for the ornithogenic soils at Hope Bay, Antarctic Peninsula. Pedon HB10 (clay, silt and sand). Mt – montmorillonite, Ta – taranakite, Le – leucophosphite, Mi – minyulite, St – struvite, Fa – fluorapatite, Me – metavariscite, Qz – quartz, K-Feld – K-feldspar, Pg – plagioclase, Mc – mica. “d” spacing in nm.

X-ray diffraction (XRD) peaks at 1.50, 1.42 and 1.00 nm indicate the presence of the clay minerals montmorillonite, vermiculite and illite, respectively. In the treatments (Fig. 2), were observed that after KCl saturation and heating to 550 °C, vermiculite was partly maintained at 1.42 nm, not completely collapsing to 1.00. This may be related to either situations: the occurrence of hydroxy-Al interlayered

2:1 clay minerals, making it difficult to decrease in the "d" spacing between the atomic planes; and 2:1 clay minerals without Al- hydroxyl interlayers, due to the competition on the part of Al for phosphates and organic matter-bound Al.

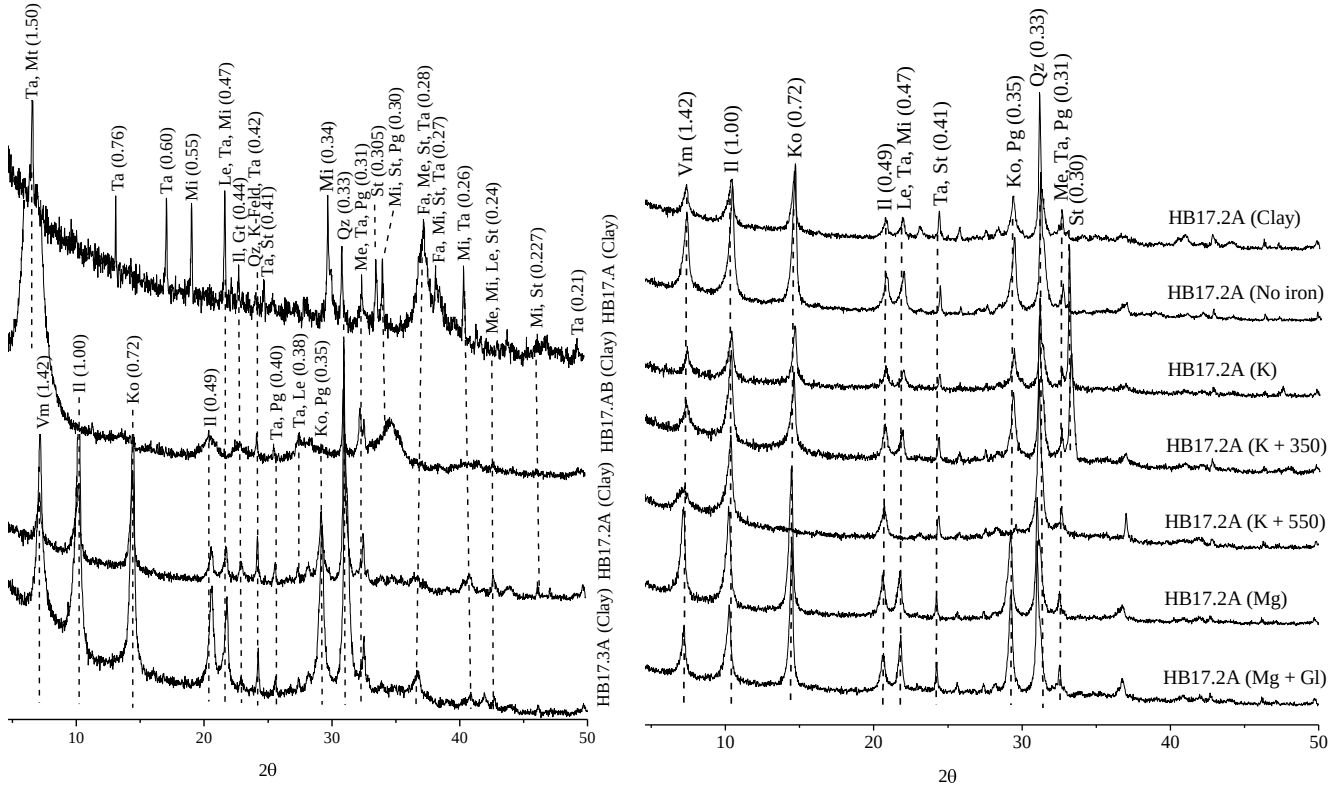


Fig. 2. XRD patterns for the ornithogenic soils at Hope Bay, Antarctic Peninsula. Pedon HB17 (clay and treatments). Mt – montmorillonite, Vm – vermiculite, Il – illite, Ta – taranakite, Le – leucophosphite, Mi – minyulite, St – struvite, Fa – fluorapatite, Me – metavariscite, Ko – kaolinite, Gt – goethite, Qz – quartz, K-Feld – K-feldspar, Pg – plagioclase, Mc – mica. “d” spacing in nm.

XRD peaks at 0.42, 0.31 and 0.30 nm indicate the presence of K-feldspar and plagioclase in the clay fraction, possibly related to lower bases and Si leaching, contributing to low chemical alteration in the thermodynamic equilibria involving Ca, Mg and K. Apart from these minerals, the presence of quartz was also detected in all soils, due to the reduced dissolution ability in the environment, associated with strong cryoclasty, favoring the mineral fragmentation and its detection in clay fraction.

Specifically in pedon HB17 (Fig. 2), the higher concentration of phosphatic minerals at the surface reveals a phosphatization process on a previously chemically depleted material with some cryoturbation and periglacial processes causing alternating concentrations of phosphatic material along the pedon. In the treatments of the clay fraction, the presence of kaolinite was confirmed by the disappearance of

XRD peaks at 0.72 nm and 0.35 nm after heating to 550 °C. Kaolinite in Antarctic soils is rather unusual, although it has been detected by Blume et al. (2002) and Simas et al. (2008) in soils of the coastal regions of Antarctica. Since the nature of the parent material of the soil of this study was sedimentary, pre-weathered and chemically poor, it seems that phosphatization occurred on previously altered material, perhaps in an environment with more favorable past conditions for chemical alterations and mineral transformation.

Vermiculite, illite, and kaolinite were detected in the non-ornithogenic HB19 pedon (Fig. 3), possibly formed in a warmer and wetter past, related to the transformation of mica and feldspar.

The detection of no clay resulting from the phosphatization process in this reference non-ornithogenic soil confirms the effect of the guano input to the formation of secondary phosphate minerals, absent here. In addition, were observed XRD peaks at 0.44 nm and 0.25 nm, referring to goethite. "Fe-oxide" was detected in some soils, probably because it is more stable in the thermodynamic equilibria of Fe, precipitating at a lower solubility constant ($10^{-44} < K_{ps} < 10^{-41}$) (Schwertmann and Taylor, 1989).

Phosphate minerals were also found in the silt fraction of the ornithogenic soils, in similar amounts (Fig. 1). Therefore, the taranakite, minyulite, leucophosphite, struvite, and fluorapatite, are found in minute microaggregates, as illustrated by Schaefer et al. (2008). The same was observed for the coarse and fine sand fractions, which apparently have similar behavior in terms of mineral occurrence, including the presence of the same phosphate minerals, as well as metavariscite (XRD peaks at 0.24, 0.28 and 0.31 nm) (Fig. 1).

In comparison, in the silt and sand fraction of the non-ornithogenic pedon mainly plagioclase and quartz were detected, which confirms the cryoclastic weathering (Fig. 3).

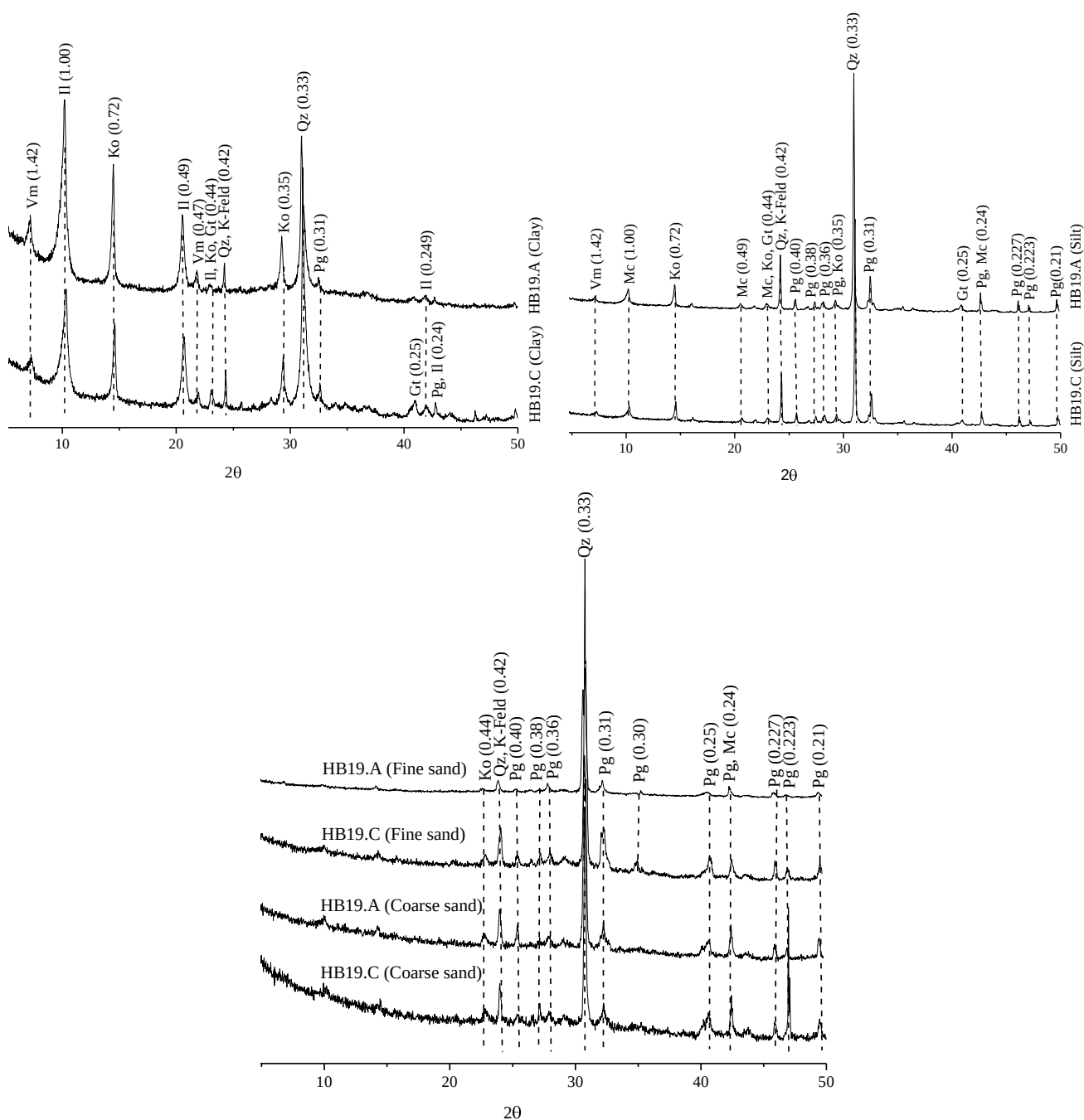


Fig. 3. XRD patterns for the some Gelisols (Criosols) at Hope Bay, Antarctic Peninsula. Pedon HB19 (clay, silt and sand). Vm – vermiculite, Il – illite, Ko – kaolinite, Gt – goethite, Qz – quartz, K-Feld – K-feldspar, Pg – plagioclase, Mc – mica. “d” spacing in nm.

Low-crystallinity Al phosphates, commonly found in ornithogenic soils of the Maritime Antarctica (Barczuk and Tatura, 2003, Schaefer et al., 2004), may be present in the soil of Hope Bay, as indicated by the high ratios of Fe_o/Fe_d and Al_o/Al_d (Table 7).

Simas et al. (2007) reported a predominance of low-crystallinity Fe minerals in the ornithogenic soils of the South Shetland archipelago, in which part of Al and

Fe may be present as organometallic complexes due to the high organic carbon content of soils.

High levels of P_2O_5 extracted with ammonium oxalate, including those with approximate results of total P_2O_5 , indicate phosphate solubilization by this extractor. This leads to an increase in the P_o/P_d ratio, causing the unrealistic impression that the phosphates are all amorphous. The narrow peak width at half height observed in the diffractograms indicates high crystallinity of the phosphates in Hope Bay.

Table 7. Fe, Al and P extracted with citrate-bicarbonate-dithionite and ammonium oxalate for < 2 mm air-dried soil samples

Pedon	Depth (cm)	-----CBD (Σ^1)-----			-----Oxalate-----			Fe _o	Al _o	P _o
		Fe ₂ O ₃	Al ₂ O ₃	P ₂ O ₅	Fe ₂ O ₃	Al ₂ O ₃	P ₂ O ₅			
		-----dag kg ⁻¹ -----								
HB1 - Ornithogenic Haploturbel										
A1	0 - 8	0.93	0.48	2.69	0.75	0.48	5.76	0.80	1.01	2.14
B2	30 - 45/50	1.66	0.97	3.43	0.91	0.95	6.19	0.55	1.03	1.80
C	90 - 130+	2.34	1.17	4.41	2.57	1.13	3.99	1.10	0.97	0.91
HB2 - Ornithogenic Haploturbel										
A	0 - 15/25	0.78	0.78	1.32	0.93	1.16	1.74	1.20	1.48	1.32
B2	30/40 - 55	0.69	0.78	1.31	0.92	1.15	1.69	1.34	1.48	1.29
C2	160 - 210	0.35	0.09	0.09	0.21	0.16	0.16	0.59	1.82	1.82
HB4 - Ornithogenic Haploturbel										
A	0 - 10	0.36	0.20	2.09	0.46	0.34	12.69	1.27	1.75	6.08
B	20 - 40	2.89	0.84	4.71	2.97	0.80	6.25	1.03	0.95	1.32
HB5 - Ornithogenic Haplohemist										
O	0-30	0.69	0.94	1.37	0.81	1.20	2.32	1.16	1.28	1.69
HB7 - Ornithogenic Haploturbel										
A	0 - 10	1.02	0.22	1.31	0.98	0.17	1.24	0.96	0.77	0.95
B2	30 - 50	1.26	0.40	1.68	0.85	0.23	1.02	0.68	0.59	0.60
B3	50 - 70	2.01	1.44	4.03	1.62	1.74	4.77	0.81	1.21	1.18
HB10 - Ornithogenic Haploturbel										
A	0 - 10	0.65	0.61	3.11	0.66	0.67	12.61	1.03	1.10	4.06
B2	45 - 90	1.44	1.60	4.39	1.06	3.49	11.87	0.74	2.18	2.70
HB11 - Ornithogenic Gelorthent										
A	0 - 10	0.73	0.46	1.16	0.92	0.62	1.44	1.26	1.35	1.24
3Ax	35 - 60	0.54	0.35	0.83	0.81	0.66	1.37	1.51	1.90	1.65
3Cx	60 - 85	0.70	0.39	1.09	0.66	0.44	1.10	0.95	1.12	1.01
4A	85 - 120	0.35	0.27	0.59	0.40	0.29	0.64	1.12	1.07	1.09
HB16 - Ornithogenic Gelorthent										
A	0 - 10	1.24	0.61	1.62	1.19	0.86	2.62	0.96	1.41	1.61
C2	29 - 50	0.44	0.70	1.86	0.58	0.81	2.56	1.31	1.16	1.38
HB17 - Ornithogenic Haploturbel										
A	0 - 10	0.31	0.19	4.81	0.45	0.42	8.42	1.44	2.19	1.75
AB	10 - 15	0.46	0.15	0.87	0.58	0.29	1.27	1.26	1.96	1.46
2A	35 - 43	0.57	0.11	0.61	0.53	0.21	0.53	0.93	1.95	0.86
3A	60 - 72	0.53	0.16	0.45	0.56	0.26	0.51	1.05	1.70	1.11
HB19 - Lithic Haploturbel										
A	0 - 10	0.48	0.10	0.01	0.11	0.09	0.06	0.23	1.53	6.18
C	30 - 60	0.46	0.10	0.01	0.13	0.10	0.07	0.29	1.69	7.52

¹ Sum of three extractions.

4. CONCLUSIONS

- In Hope Bay, lower temperatures throughout the year and reduced moisture in the summer when compared with the South Shetland Islands result in lower diversities of plant communities, although soil organic matter reaches similar amounts with Maritime Antarctic soils. Vegetation is restricted to no more than occasional nuclei of crusty lichens, green algae (*Prasiola crispa*) and few mosses.
- Factors such as the low rate of guano decomposition, low leaching of bases, mainly of Ca, and low organic matter, contribute to little soil acidification and low exchangeable Al^{3+} levels, which was very contrasting with ornithogenic soils from Maritime Antarctic.
- A mineral assemblage representative of phosphatization, such as taranakite, minyulite, leucophosphite, struvite, and fluorapatite, were detected. In Hope Bay, they seem to be immobilized for a longer time, due to the slow action of the processes involving dissolution, neoformation of secondary phosphate minerals, and leaching.
- The ornithogenesis represents an important mechanism of nutrient transfer from the sea to the continent, with enrichment of the terrestrial ecosystems, otherwise developed chemically poor parent materials.
- The presence of kaolinite indicate deeper weathering under wetter (warmer?) condition in the past, with greater chemical and mineralogical changes in Hope Bay. Hence, the current environment is subjected to phosphatization on pre-weathered, sedimentary material.

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CHAPTER 5

Micromorphological and microchemical indicators of pedogenesis in Ornithogenic Cryosols (Gelisols) of Hope Bay, Antarctic Peninsula

ABSTRACT

PEREIRA, Thiago Torres Costa. **Micromorphological and microchemical indicators of pedogenesis in Ornithogenic Cryosols (Gelisols) of Hope Bay, Antarctic Peninsula.** Viçosa: UFV, 2012. Cap. 5 (Tese – Doutorado em Solos e Nutrição de Plantas).

Micromorphological investigations of Antarctic soils are comparatively scarce, and could help understand the genesis of cryogenic soils under extreme polar conditions under little influence of biotic factors. In most areas of Maritime Antarctica, the soil microstructure is apparently influenced by the local lithology and deposition of bird guano. The present study was carried out in Hope Bay, in the northern part of the Antarctic Peninsula, possibly one of the oldest sites of penguin occupation in the region. We describe and analyze the most important micro and sub-microscopic features of selected Ornithogenic Cryosols (Gelisols) from this part of Antarctic Peninsula, representing a transitional climatic zone between the wetter South Shetlands and the much drier Weddell Sea sector. Nine pedons representing the main ornithogenic soils found in ice-free areas of Hope Bay were selected for the micromorphological study. Undisturbed soil blocks were sampled at different depths, ranging between 0 and 30 cm. The microstructure and sub-microstructure were further investigated using a JEOL 8200 and a Zeiss scanning electron microscopes, both coupled with an microprobe (SEM/WDS). These pedons have a very limited surface accumulation of organic matter formed by mosses and lichens, changing abruptly to a mineral phosphatic horizon of bleached colours, and usually hard-cemented. A small to medium-sized granular structure is generally observed, with ovoidal, subrounded forms, including several well-defined ornithogenic materials, such as P-rich organic remains, nodular phosphates forms and minute fragments of

bone apatite. The chemical composition of several features indicates the presence of discrete forms of taranakite, minyulite, leucophosphite, struvite and fluorapatite, typical of phosphatization process in this zone. The process enhances chemical alteration of the substrate and is one of the main soil-forming process in ornithogenic soils, resulting in P-rich ovoidal aggregates. P-rich solutions penetrate desiccation fractures and cleavage planes in large clasts and react preferably with plagioclases. P reacts with Al and Fe to form various amorphous and crystalline P phases. Permafrost cementation of deeper phosphate layers indicate that warmer/wetter conditions occurred in the past, during which P was leached downwards and reacted with the rock substrates, developing stable ovoidal aggregates, now incorporated in dry-cemented substrate horizon.

RESUMO

PEREIRA, Thiago Torres Costa. **Indicadores micromorfológicos e microquímicos de pedogênese em Criossolos Ornitogênicos (Gelissolos) de Hope Bay, Antártica Península.** Viçosa: UFV, 2012. Cap. 5 (Tese – Doutorado em Solos e Nutrição de Plantas).

Investigações micromorfológicas de solos da Antártica são escassas e podem contribuir para o entendimento da gênese de solos criogênicos sob extrema condição polar e sob pouca influência de fatores bióticos. Na maior parte da Antártica marítima, a microestrutura do solo é aparentemente influenciada pela litologia local e deposição de guano por pinguins. O presente estudo foi realizado em Hope Bay, no extremo norte da Península Antártica, possivelmente um dos sítios mais antigos de ocupação por pinguins na região. Foram descritas, coletadas e analisadas importantes feições micro e sub-microscópicas de Criossolos (Gelissolos) Ornitogênicos desta parte da Península, que representa uma zona de transição climática entre as Ilhas Shetlands do Sul, úmidas, e o Mar de Weddell, seco. Nove perfis representativos de solos ornitogênicos encontrados nas áreas livres de gelo de Hope Bay foram selecionados para os estudos micromorfológicos. Amostras indeformadas de solos foram coletadas, cujas profundidades variaram entre 0 e 30 cm. As microestruturas foram estudadas utilizando um microscópio eletrônico de varredura (JEOL 8200) com microsonda acoplada (*wavelength dispersive spectrometry*). Todos os perfis possuem limitada superfície de acumulação de matéria orgânica formada por musgos e líquens, que transicionam abruptamente para um horizonte fosfático acinzentado, e usualmente cimentado. A estrutura é normalmente pequena/média, com formas ovóides subarredondadas, que incluem materiais ornitogênicos bem definidos como remanescentes orgânicos ricos em P, formas de fosfatos nodulares e fragmentos de apatita de osso. A composição química de muitas feições indica a presença de discretas formas de taranakita, miniulita, leucofosfita, estruvita e fluorapatita, típicas do processo de fosfatização. O processo aumenta a alteração química do substrato e é um dos principais processos de formação dos solos em sítios de ornitogênese, resultando em agregados ovóides ricos em P. Nestes casos, soluções ricas em P penetram em fraturas de dissecação e planos de clivagem em fragmentos maiores, reagindo preferencialmente com os plagioclásios. P reage também com Al e Fe para

formar várias fases fosfáticas cristalinas e amorfas. A cimentação do permafrost em camadas fosfáticas mais profundas nos perfis indicam condições mais quentes e úmidas no passado, em que lixiviados ricos em P reagiram com substratos rochosos nestes locais, desenvolvendo agregados arredondados atualmente presentes nestes horizontes.

1. INTRODUCTION

Micromorphological investigations of Antarctic soils are few (van Vliet-Lan   et al., 2004). Pioneering works on the micromorphology of the Antarctic soils was made by Fitzpatrick (1956) and Kubiena (1970). Micromorphological analysis makes it possible to study the interrelationships between the various individual components, particles, and pores that make up sediments and soils. With regard to Antarctic soils, the micromorphological and microchemical studies can reveal important information regarding soil genesis and physic-chemical behavior (Schaefer et al., 2008).

At present, rock-inherited features and secondary clays dominate cold regions and mountain soils, which also are subject to cryoturbation processes and reduced rates of soil development (van Vliet-Lan   et al., 2004). Therefore, the microstructure development is greatly influenced by the local lithology, and, in some cases, by the deposition of large amounts of guano. Different types of platy and granular fabrics (van Vliet-Lan  , 1985; Schaefer et al., 2008) and eluviation-illuviation processes (Fox and Protz, 1981) are commonly reported in cryogenic soils from different polar environment.

A granular microstructure comprised of a granic/granoidic fabric is commonly observed in surface horizons and is replaced by a coalesced microstructure at depth (Smith et al., 1991; Tarnocai et al., 1993; White and Fox, 1997; Schaefer et al., 2008), also orbiculic fabric (van Vliet-Lano   et al., 2004). Platy structure having a banded fabric occurs in Cryosols subjected to freezing and thawing processes (van Vliet-Lan  , 1985). Despite one the oldest human-visited region in Antarctica, no detailed pedological on microprobe studies have been conducted in Cryosols from the Antarctic Peninsula. However, this area has a transitional climate between the dry, cold Polar Desert of the Weddell Sea islands and the warmer, wettest South Shetlands.

Soils from Maritime Antarctica are generally more developed than those from drier and colder climatic zones of Antarctica (Blume et al., 2004; Michel et al., 2006). In Hope Bay, were identified and characterized five main soil units, and the most important being: i) Turbic Cryosol (Ornithic) - (Ornithogenic Haploturbel); and ii) Turbic Cryosol (Lithic) - (Lithic Haploturbel).

Although periglacial, physical weathering is undoubtedly a major soil-forming process in the part of Antarctica, chemical weathering also occurs, notably in ornithogenic soils (Michel et al., 2006; Simas et al., 2006). The latter soils are strongly affected by sea-land transfers of nutrients by birds, mostly penguins, through deposition of large amounts of guano during the austral summer. The fine fraction of these soils contains mainly phosphates of various chemical and mineral compositions (Tatur and Keck, 1990). In these soils, a particular and complex process of deep soil phosphatization occurs, which has been described in detail by Tatur and Barczuk (1985), Tatur (1989), Schaefer et al. (2004), and Simas et al. (2007).

The present study was carried out in Hope Bay, in the northern part of the Antarctic Peninsula, possibly one of the oldest sites of penguin occupation in the region. It was aimed to describe and analyze the most important micro and sub-microscopic features of selected ornithogenic soils from this part of Antarctic Peninsula, representing a transitional climatic zone between the humid South Shetlands and the much drier Weddell Sea sector.

2. MATERIAL AND METHODS

2.1. Study area

The study was conducted in Hope Bay, in the Northern end of the Antarctic Peninsula. The study area is bordered in the South by Mount Flora (520 m asl) and in the East by the Buenos Aires glacier, whose snout reaches over 100 m. Scar (2002) defined the area of Mount Flora and surroundings as an Antarctic Specially Protected Area (ASPA 148). Excluding Mount Flora, the ice-free area between the sea and the glaciers covers a region of approximately 3 km², with average elevations of ≤ 100 m (Birkenmajer, 1993a, Martin-Serrano et al., 2005).

According to Köppen's classification, the region is part of the EF (polar) climate. The average temperature of Hope Bay measured at Esperanza Station, between 1952 and 2010 was -5.1 °C, with annual precipitation of approximately 150 mm, characterizing a semi-desert climate.

The geology of Hope Bay is composed of a metasedimentary (Trinity Peninsula Group - Hope Bay Formation: marine siliciclastic turbidites and sandstones), sedimentary (Botany Bay Group - Mount Flora Formation: sandstones, conglomerates and schists) and volcanic rock sequences (Antarctic Peninsula Volcanic Group - Kenney Glacier Formation: rhyolite-dacites, ignimbrites, conglomerates and cemented tuff) (Birkenmajer 1993b; del Valle et al. 2001; Scar, 2002).

The geomorphology is related to both paraglacial and periglacial processes and landforms, reflecting the widespread late Quaternary retreat of glaciers (Martín-Serrano et al., 2005), with shorter intervals of minor glacial advances. Most geomorphic processes are related to the coastal environmental, with persistent winds, summer melting, and increasing periglacial erosion, specially thermokarst features.

2.2. Soil sampling

Nine pedons representing the main ornithogenic soils found in ice-free areas of Hope Bay were selected for the micromorphological study, and all were classified as Cryosol/Gelisol, except for pedon 16. Detailed chemical, physical and

mineralogical data regarding these soils are found in chapters 2 and 3 this issue. The soil depths considered in the micromorphological analyses were 0-30 cm for all pedons.

2.3. Micromorphology

Undisturbed soil blocks were sampled at different depths, within the reach 30 cm from the surface. All samples were dried at 50 °C and impregnated with a 1:1 crystic resin:styrene mix poured onto sample at vacuum. Impregnated samples were cut into slabs of 0.5 cm thickness using a diamond saw, and polished with corundum and diamond abrasives from 250 down to 600 mesh. After ultrasonic cleaning, the polished blocks were mounted onto glass slides followed by polishing and hand-finishing to produce 30 µm thick, 10 × 6 cm sized, thin-sections. No cover slips were used, and fine ultrapolishing using diamond powder of decreasing size (60 to 1 µ) ensured that a final flat surface was produced. Thin-sections were examined under a Zeiss polarizing microscope (OTM level) using an attached Pentax camera fitted with a Zeiss exposure meter. Pedological features of the soil horizons at OTM level were analysed using standard micromorphological techniques (Bullock et al., 1985). Selected areas described under the petrographic microscope (OTM) were submitted to SEM/WDS analysis in carbon-coated specimens, at high resolution.

2.4. Sub-microscopy and electron microscopy analysis: SEM/WDS

In all carbon-coated soil thin-sections, the microstructure and sub-microstructure were further investigated using a JEOL 8200 and a Zeiss scanning electron microscopes, both coupled with an Oxford energy dispersive X-ray detector (SEM/WDS), following the recommendations of Bisdom and Ducloux (1983). Microchemical analyses were acquired at 17 to 18 mm working distance and 15 kv accelerating voltage.

3. RESULTS AND DISCUSSION

These pedons represent typical ornithogenic soils from the Antarctic Peninsula. They have a surface accumulation of organic matter formed by discontinuous mosses and lichens, changing abruptly to a mineral phosphatic horizon of bleached colours, and usually cemented. Some characteristics of soils studied are illustrated in table 1.

In general, the soils have a weak to moderate structural development, varying primarily between subangular blocky and granular. Soils microfabric have a moderate or strong structural development. At this scale, a small to medium-sized granular structure is generally observed, with rounded to subrounded forms, including several well-defined ornithogenic pedofeatures, such as P-rich organic remains, nodular phosphates forms and minute fragments of bone apatite (Fig. 1), with chemical composition presented in table 2. The microstructure is typically orbiculing, ovoidal-shaped, consistent with that described by van Vliet-Lanoë et al. (2004) for cryogenic fabrics of Cryosols from Canada. These materials are usually surrounded by secondary, concentric illuvial pedogenic P deposition. van Vliet-Lanoë (1985) and Schaefer et al. (2004) noted that phosphatic coatings, formed as a result of pressured ultra-desiccation of the colloids during the freezing process, make the granular units resistant to cryoturbation effects, mass wasting stresses, and collapse on thawing.

Fragments of plagioclases and quartz in all soils occur in varying size ranges (< or > 2 mm), indicating the effectiveness of physical weathering and particle size reduction through freeze-and-thawing processes in Hope Bay.

The highly diverse size of clasts and grains indicate that this soil is formed from extensive mechanical reworking. This is expected in this part of Antarctica, as a result of solifluction, cryoturbation and other periglacial process normally occurring in Turbels (Schaefer et al., 2008).

Table 1. Some structural and microstructural characteristics of pedons studied

Pedon	Classification	Structure ¹	Microstructure ²	P ³	Main phosphatic minerals (clay fraction)
1	Ornithogenic Haploturbel	w m gr	Type: granular Form: equidimensional and triaxial Degree of rounding: rounded Surface roughness: smooth Relative distribution: enaulic/gefuric Degree of aggregate development: moderate/strong Pores: complex	6010.6	Taranakite, minyulite, leucophosphate, fluorapatite
3	Ornithogenic Haploturbel	st m gr	Type: granular Form: equidimensional and triaxial Degree of rounding: subrounded Surface roughness: smooth Relative distribution: gefuric/chitonic Degree of aggregate development: strong Pores: complex	7149.6	Taranakite
4	Ornithogenic Haploturbel	md/st m gr	Type: granular Form: equidimensional Degree of rounding: subrounded Surface roughness: wavy Relative distribution: chitonic Degree of aggregate development: strong Pores: complex	7149.6	Taranakite
7	Ornithogenic Haploturbel	md/st m gr	Type: granular Form: equidimensional Degree of rounding: subrounded Surface roughness: smooth Relative distribution: gefuric Degree of aggregate development: weak/moderate Pores: complex	7237.3	Taranakite, leucophosphate, struvite, fluorapatite
14	Ornithogenic (Anthropic) Haploturbel	w f gr/sg	Type: granular Form: equidimensional and triaxial Degree of rounding: subrounded Surface roughness: smooth Relative distribution: gefuric Degree of aggregate development: strong Pores: complex	996.3	Taranakite, minyulite, leucophosphate, struvite, fluorapatite
15	Ornithogenic (Anthropic) Haploturbel	w f gr/sg	Type: granular Form: equidimensional and triaxial Degree of rounding: subrounded Surface roughness: smooth Relative distribution: gefuric Degree of aggregate development: moderate Pores: complex	586.4	Taranakite, minyulite, leucophosphate, struvite, fluorapatite
16	Ornithogenic Gelorthent	sg	Type: maciça Form: equidimensional and triaxial Degree of rounding: subrounded Surface roughness: smooth Relative distribution: porphyric Degree of aggregate development: weak Pores: complex	5765.3	Taranakite, minyulite, fluorapatite
17	Ornithogenic Haploturbel	-	Type: granular Form: equidimensional Degree of rounding: subrounded Surface roughness: wavy Relative distribution: chitonic Degree of aggregate development: strong Pores: complex	5527.3	Taranakite, leucophosphate, minyulite, struvite, fluorapatite

¹Development: w = weak, md = moderate, st = strong. Size: f = fine, m = medium. Type: gr = granular, sg = single grain;

²According Brewer (1964), Stoops and Jongerius (1977), Bullock et al. (1985); ³P Mehlich-1 mean.

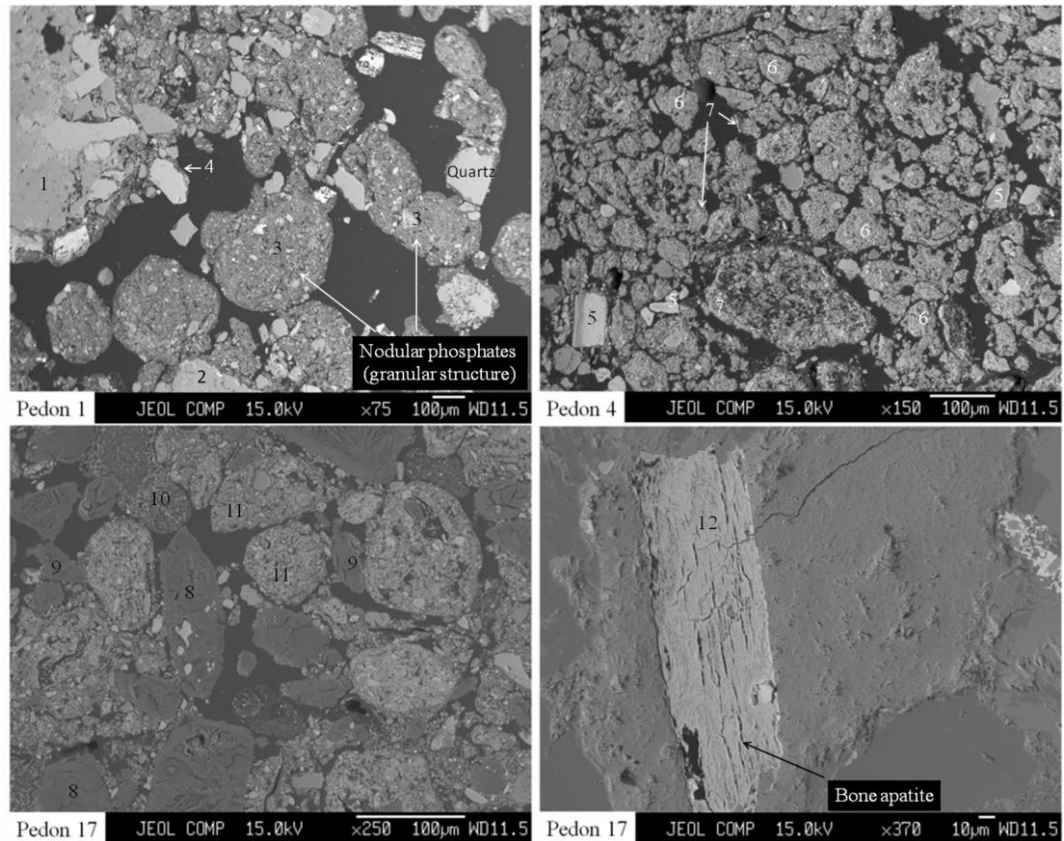


Fig. 1. SEM images showing a well-developed granular structure and bone apatite fragments observed in pedons studies.

Table 2. WDS analysis of micropedological features observed in pedons studied

Pedofeature	n	CaO	MgO	Na ₂ O	K ₂ O	SiO ₂	Al ₂ O ₃	P ₂ O ₅	Fe ₂ O ₃	F	Total
-----%-----											
Pedon 1 - Ornithogenic Haploturbel											
1 ^a Na-Plagioclase	4	0.5±0.1	nd	11.1±0.9	0.4±0.5	69.8±0.8	19.9±0.6	nd	nd	nd	101.8±1.6
2 ^a K-Plagioclase	2	nd	nd	0.9±0.7	15.1±1.2	66.9±0.5	17.7±0.2	nd	0.1±0.0	nd	101.8±0.2
3 ^a Fluorapatite	13	45.4±8.9	0.6±0.3	0.8±0.7	nd	nd	nd	18.3±2.9	1.9±0.9	1.4±0.3	68.5±10.4
4 ^a Leucophosphite	4	1.6±1.0	0.2±0.1	0.1±0.1	0.9±0.2	5.2±2.4	5.3±0.5	13.0±1.3	14.1±1.7	0.3±0.2	40.8±2.1
Pedon 4 - Ornithogenic Haploturbel											
5 ^a Na-Plagioclase	5	0.8±0.7	0.1±0.1	10.1±2.0	1.2±1.3	66.0±4.5	21.2±1.5	nd	0.1±0.0	nd	99.2±3.9
6 ^a Fluorapatite	17	41.4±5.5	0.4±0.1	0.6±0.2	0.1±0.0	0.9±0.8	1.0±0.3	15.3±2.4	0.4±0.1	1.1±0.2	61.0±7.2
7 ^a Leucophosphite	1	2.7	0.4	0.4	1.1	0.4	1.5	13.4	19.6	nd	39.5
Pedon 17 - Ornithogenic Haploturbel											
8 ^a K-Plagioclase	4	0.0±0.0	nd	0.5±0.2	15.7±0.2	67.3±0.7	18.4±0.2	nd	0.0±0.0	nd	102.0±0.7
9 ^a Na-Plagioclase	2	0.7±0.2	0.2±0.2	9.3±0.1	1.6±0.4	67.2±0.1	21.8±0.2	nd	0.3±0.1	nd	101.1±0.1
10 ^a Struvite	7	0.8±1.3	21.4±2.0	0.1±0.1	0.0±0.0	0.7±1.6	0.2±0.1	17.4±1.7	0.1±0.0	0.2±0.1	40.9±0.9
11 ^a Taranakite	2	0.3±0.1	0.3±0.1	0.0±0.0	6.5±0.0	0.4±0.1	28.0±1.1	18.6±0.6	0.7±0.1	0.9±0.3	55.8±1.9
12 ^a Bone apatite	10	43.9±5.3	1.5±0.5	0.6±0.3	0.3±0.2	2.7±2.0	2.1±1.4	16.6±1.3	0.8±0.4	1.1±0.3	69.2±5.6

n: number of analysis; nd: not determined; ^a Illustrated in Fig. 1

The sub-angular characteristic of sand-sized and coarser particles indicate short-distance transport and physical disruption following thermal microcracking, some with illuvial deposition of phosphates (Fig. 2). The chemical composition of selected pedofeatures are presented in table 3.

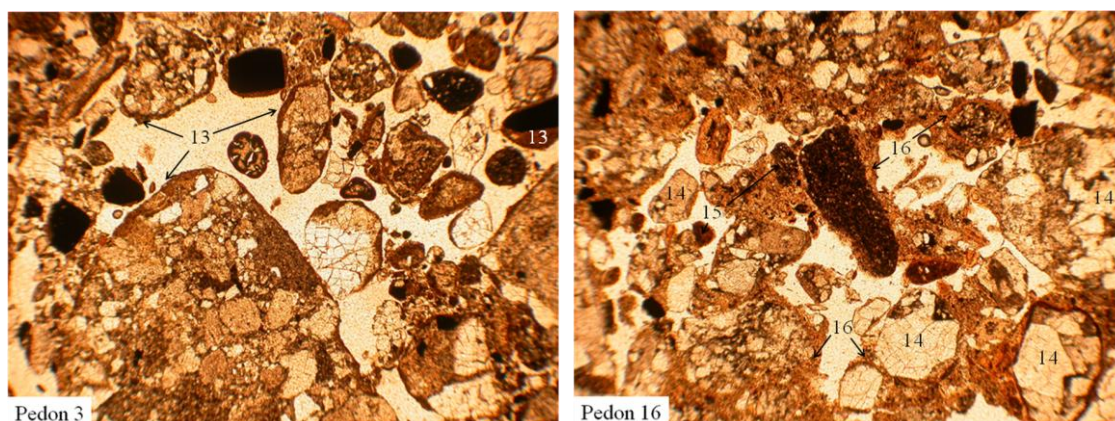


Fig. 2. OTM images showing granular structure in small aggregates. Illuvial deposition of phosphate filling microcracks in the sand-sized particles.

Table 3. WDS analysis of micropedological features observed in pedons studied

Pedofeature	n	CaO	MgO	Na ₂ O	K ₂ O	SiO ₂	Al ₂ O ₃	P ₂ O ₅	Fe ₂ O ₃	F	Total
-----%-----											
Pedon 3 - Ornithogenic Haploturbel											
13 ^b Illuvial phosphate	7	26.2±5.8	1.7±0.3	0.5±0.2	0.4±0.2	4.7±2.1	2.6±1.4	12.0±1.2	1.1±0.8	0.8±0.3	50.2±8.4
Pedon 16 - Ornithogenic Gelorthent											
14 ^b Na-Plagioclase	1	0.2	0.1	5.0	0.2	86.6	8.0	nd	1.8	nd	101.9
15 ^b Fe(OH) ₃ form with P	11	0.8±0.1	0.4±0.0	0.4±0.1	nd	0.8±0.4	1.3±0.6	4.3±0.4	88.3±1.8	nd	96.6±0.9
16 ^b Illuvial phosphate	25	41.4±3.8	0.6±0.1	0.9±0.1	0.3±0.2	1.4±1.0	4.0±0.8	18.0±1.8	2.4±1.3	1.4±0.3	70.7±4.2

n: number of analysis; nd: not determined. ^b Ilustrated in Fig. 2.

Increasing roundness of lithorelicts with decreasing particle size reflects the effects of differential frost heaving and intense cryoturbation during freeze-and-thawing cycles, creating ovoidal, granular-shaped, stable peds.

At the OTM level, illuvial phosphatic features occur as bright yellow infillings along cleavage lines or broken, cryoturbic fragments of rocks and aggregates, with good orientation (Fig. 3).

The P-rich solution penetrates in the cracks and cleavage planes and reacts preferentially with plagioclases forming a framework of phosphatic rims around these materials. According to Schaefer et al. (2008), this reaction with P-rich solutions leads to the progressive displacement of Si from rock minerals, and consequently, enhanced chemical weathering.

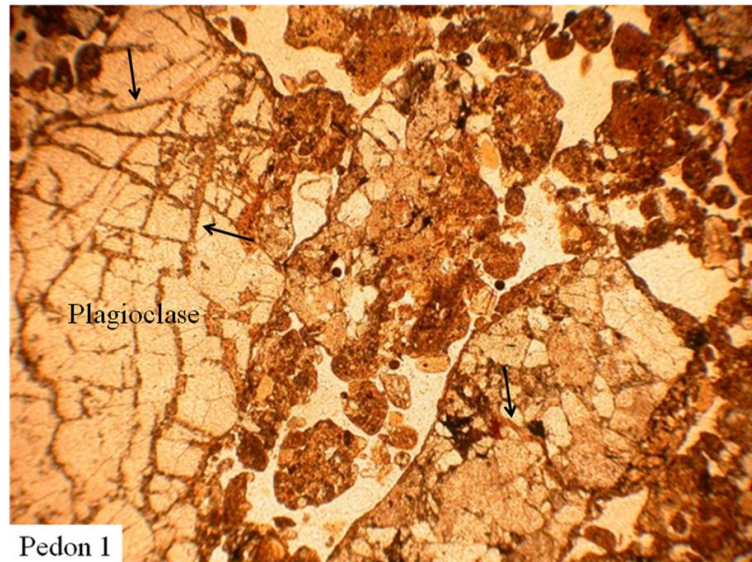


Fig. 3. OTM images showing illuvial phosphatic features in cryoturbic fragments indicated by black arrows. The WDS mean results were 16.8% P_2O_5 for these illuvial phosphates.

Based on microchemistry mapping, the fine material is dominated by phosphatic aggregates (Fig. 4 to Fig. 8). In all pedons, phosphatization process occurs throughout, with a combination of P-Al-Fe phases mainly, but also P-Ca, P-Mg.

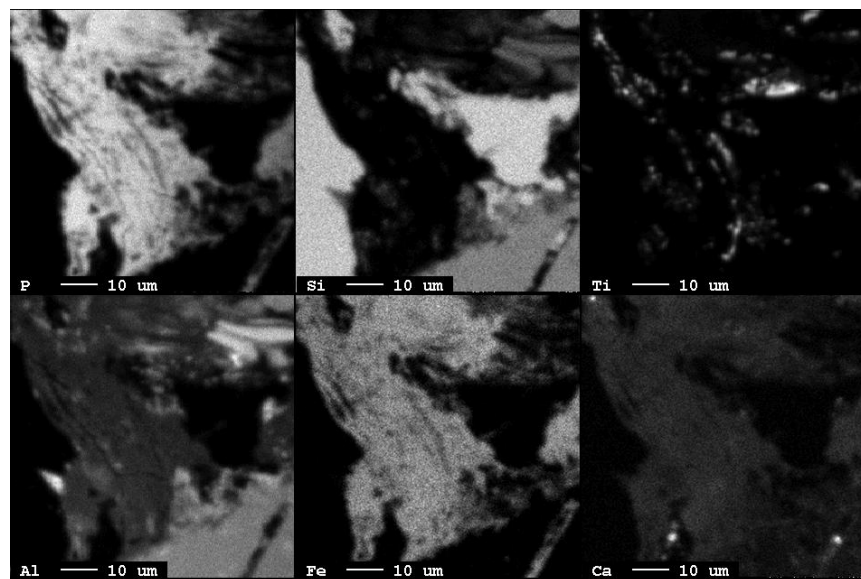


Fig. 4. Qualitative WDS analysis showing phosphatic soil matrix, probably with leucophosphite, fluorapatite, taranakite and minyulite (pedon 1).

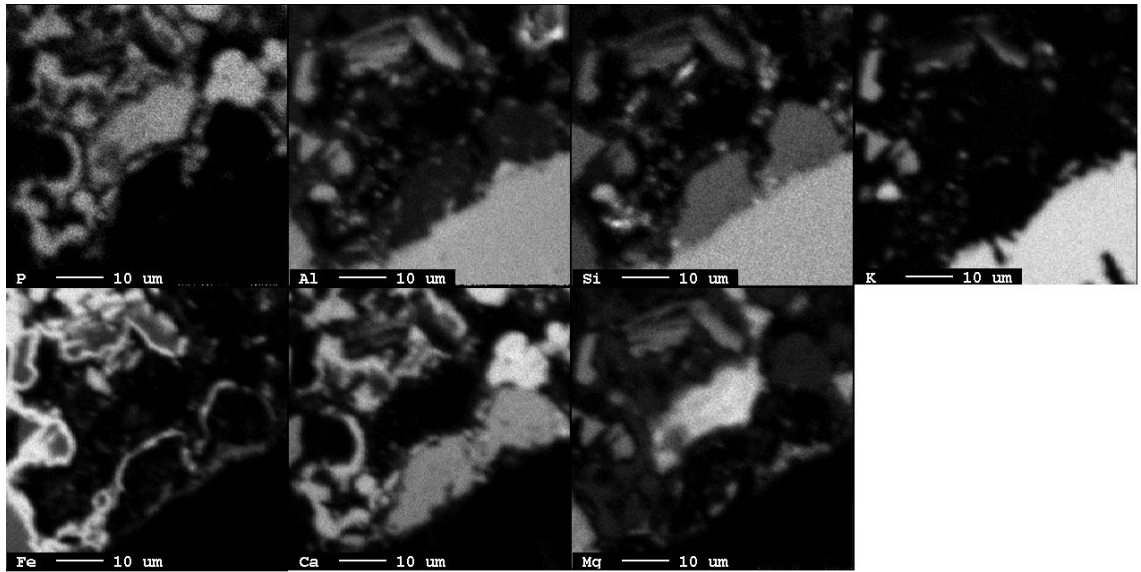


Fig. 5. Qualitative WDS analysis showing phosphatized rock with fluorapatite, struvite, and leucophosphite, based on chemical composition of phosphatic zones (pedon 7/rock).

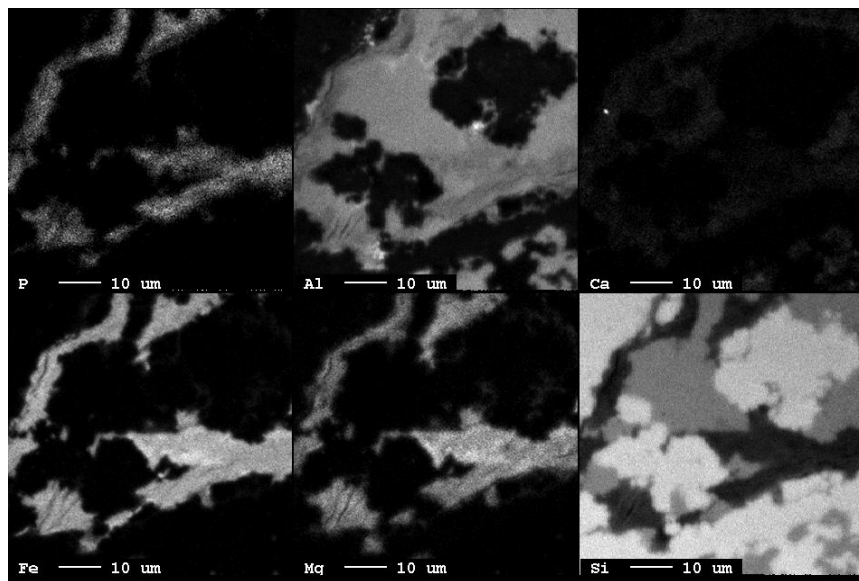


Fig. 6. Qualitative WDS analysis showing microfabric with coatings of taranakite, leucophosphite and struvite (pedon 14).

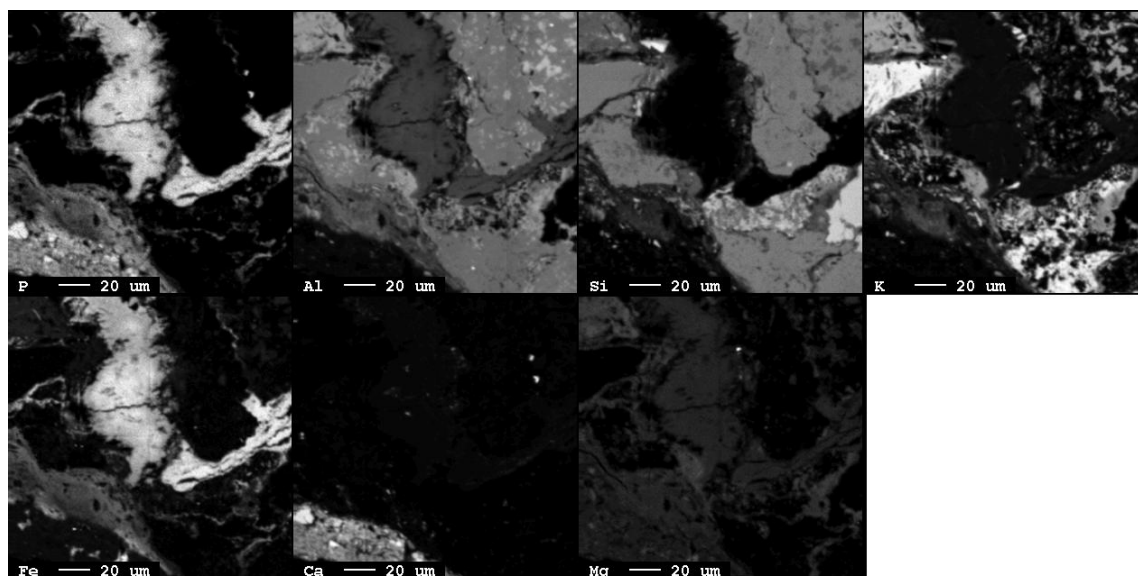


Fig. 7. Qualitative WDS analysis showing clasts filled with leucophosphite (mainly), and fluorapatite, taranakite, minyulite, struvite (pedon 17).

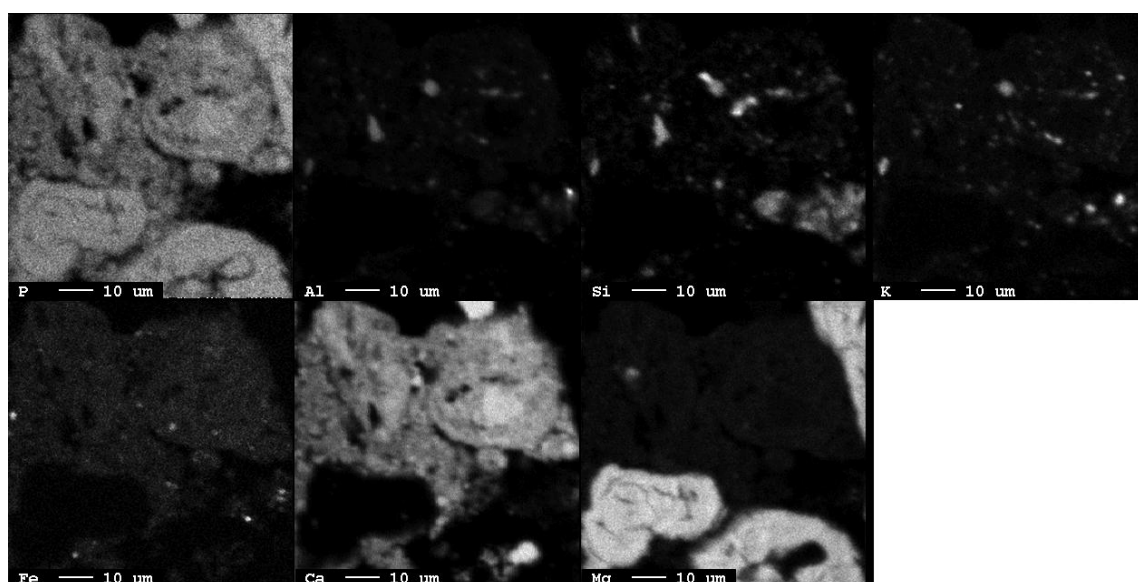


Fig. 8. Qualitative WDS analysis showing subrounded forms of struvite and fluorapatite in pedon 17.

The chemical composition of the secondary phosphate reflects the nature of the lithofragment that is phosphatized (Table 4). The clasts and grains are composed almost exclusively of plagioclases and quartz, so that Al and Si released from acidolysis. The chemical alteration of the grain leads to P reacting with Al and Fe to form various amorphous and crystalline P phases. According to Blume et al. (2004) and Simas et al. (2006), non-crystalline phases are important soil components and reach > 75 % of the clay fraction for some ornithogenic soils. Following reaction, the

newly formed P-Al-Fe forms are concentrated in infillings or as illuvial coating, creating the typical P-rich ovoidal aggregates by ultra-desiccation.

Transects analyzes were made from the fine soil matrix to the primary Al-silicates that compose the clasts (Fig. 9 and Fig. 10). Si and Al peaks increasing intensity indicates the presence of Al-silicates. The P reaction, associated with Ca, Fe, Mg and K concentration, occurs on the edges or within primary minerals, suggesting that P-rich liquid leachates have throughout soaked the clasts, before were eventually dried-up by freezing and desiccation.

Table 4. WDS analysis of micropedological features observed in pedons studied

Pedofeature	n	CaO	MgO	Na ₂ O	K ₂ O	SiO ₂	Al ₂ O ₃	P ₂ O ₅	Fe ₂ O ₃	F	Total
-----%-----											
Pedon 7 - Ornithogenic Haploturbel											
Fluorapatite	1	58.5	nd	0.1	0.0	0.6	0.6	21.7	0.1	1.5	83.1
Al-silicate (P-Fe-K)	1	3.1	5.4	1.3	7.4	34.1	12.1	6.3	9.1	0.1	78.8
Pedon 7 / rock fragment											
K-Plagioclase	5	0.1±0.1	0.2±0.2	0.5±0.6	15.5±0.7	66.9±0.5	18.5±0.2	nd	0.6±0.3	nd	102.5±0.2
Ca-Na-Plagioclase	2	5.2±1.2	0.0±0.0	6.9±2.1	0.2±0.1	68.4±6.1	20.4±4.9	nd	1.0±1.2	nd	102.0±1.4
Na-Plagioclase	1	0.5	nd	10.9	0.1	70.0	20.0	nd	0.1	nd	101.6
Al-silicate (Fe-Mg)	3	0.2±0.0	17.2±0.6	0.0±0.0	0.9±0.7	29.9±1.3	19.2±1.9	nd	16.4±1.4	nd	84.8±1.2
Fe(OH) ₃ forms with P	10	1.6±0.3	1.3±0.4	0.4±0.1	0.7±0.5	2.1±0.9	5.1±0.7	3.1±0.3	61.0±2.4	0.1±0.1	75.5±3.0
Fluorapatite	2	53.1±4.8	1.8±1.9	0.7±0.7	0.1	0.3±0.2	0.2±1.2	21.4±0.2	1.1±0.9	0.9±0.0	80.0±2.5
Pedon 14 - Ornithogenic (Anthropic) Haploturbel											
Na-Plagioclase (P)	1	0.4	0.4	9.1	0.7	67.0	15.1	0.8	1.0	0.0	94.5
K-Plagioclase	1	nd	nd	0.3	15.9	66.8	18.1	nd	0.0	nd	101.2
Illite	3	0.2±0.0	2.8±0.3	0.4±0.6	8.6±0.8	51.4±3.5	26.8±5.0	nd	1.9±0.2	0.0±0.0	92.2±3.2
Fluorapatite	2	56.3±1.5	0.5±0.3	0.2±0.0	nd	nd	nd	21.8±0.1	0.3±0.0	1.4±0.0	80.7±1.1
Fe(OH) ₃ forms with P	2	0.2±0.0	0.1±0.0	0.2±0.2	0.2±0.1	5.7±1.8	1.8±1.0	6.0±2.2	67.7±5.5	nd	81.9±3.7
Al-silicate (P-Fe-Mg)	11	0.4±0.2	6.4±0.6	0.4±0.2	1.4±0.1	32.8±5.5	14.9±0.0	4.1±1.6	14.2±2.0	nd	74.9±0.8
Pedon 15 - Ornithogenic (Anthropic) Haploturbel											
Plagioclase with Fe-Mg	1	8.5	4.8	2.4	2.0	50.9	17.5	nd	10.4	nd	99.0
Ca-Plagioclase with Fe	3	22.8±0.4	0.1±0.0	0.0±0.0	0.0±0.1	39.3±0.5	25.0±1.0	nd	9.8±0.4	nd	97.4±1.4
Ca-Na-Plagioclase	3	12.5±2.2	0.1±0.0	4.4±1.3	0.2±0.1	54.4±2.6	29.8±1.8	nd	0.9±0.1	nd	102.4±0.2
Fe(OH) ₃ form*	1	1.4	1.1	0.3	nd	31.8	8.0	1.0	54.6		98.2
Fe(OH) ₃ form **	18	0.2±0.0	0.0±0.0	0.0±0.0	nd	0.2±0.1	0.4±0.2	1.8±0.2	89.5±2.2	nd	92.3±2.3
Fe(OH) ₃ form ***	1	0.1	0.0	nd	nd	1.0	nd	0.6	96.9	nd	98.7
Al-silicate (Na-Fe)	2	0.4±0.1	1.3±0.5	4.4±0.9	1.3±0.4	45.3±4.9	11.8±4.7	0.7±0.6	23.0±6.9	0.1±0.0	88.3±4.5

n: number of analysis; nd: not determined. Sequence: *soil matrix near Fe(OH)₃ form; ** Fe(OH)₃ form's edge; ***inside Fe(OH)₃ form.

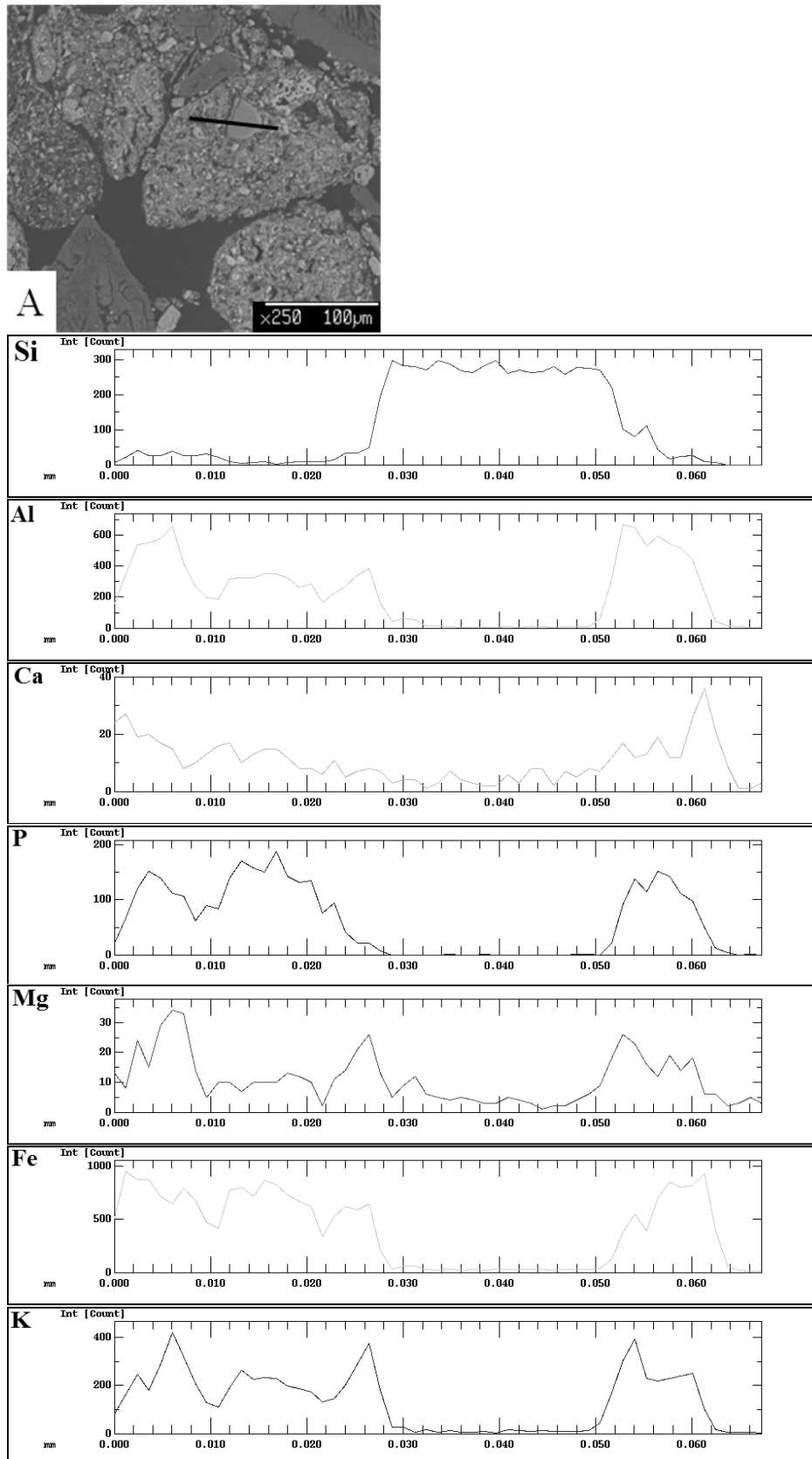


Fig. 9. Transect analysis in microfabric with phosphatic minerals (taranakite, minyulite, struvite, fluorapatite and leucophosphate). P detection at the edges of silicates (comparing P-Si) can indicate reaction due chemical attack (pedon 15). Black line in image A show where the transect was performed.

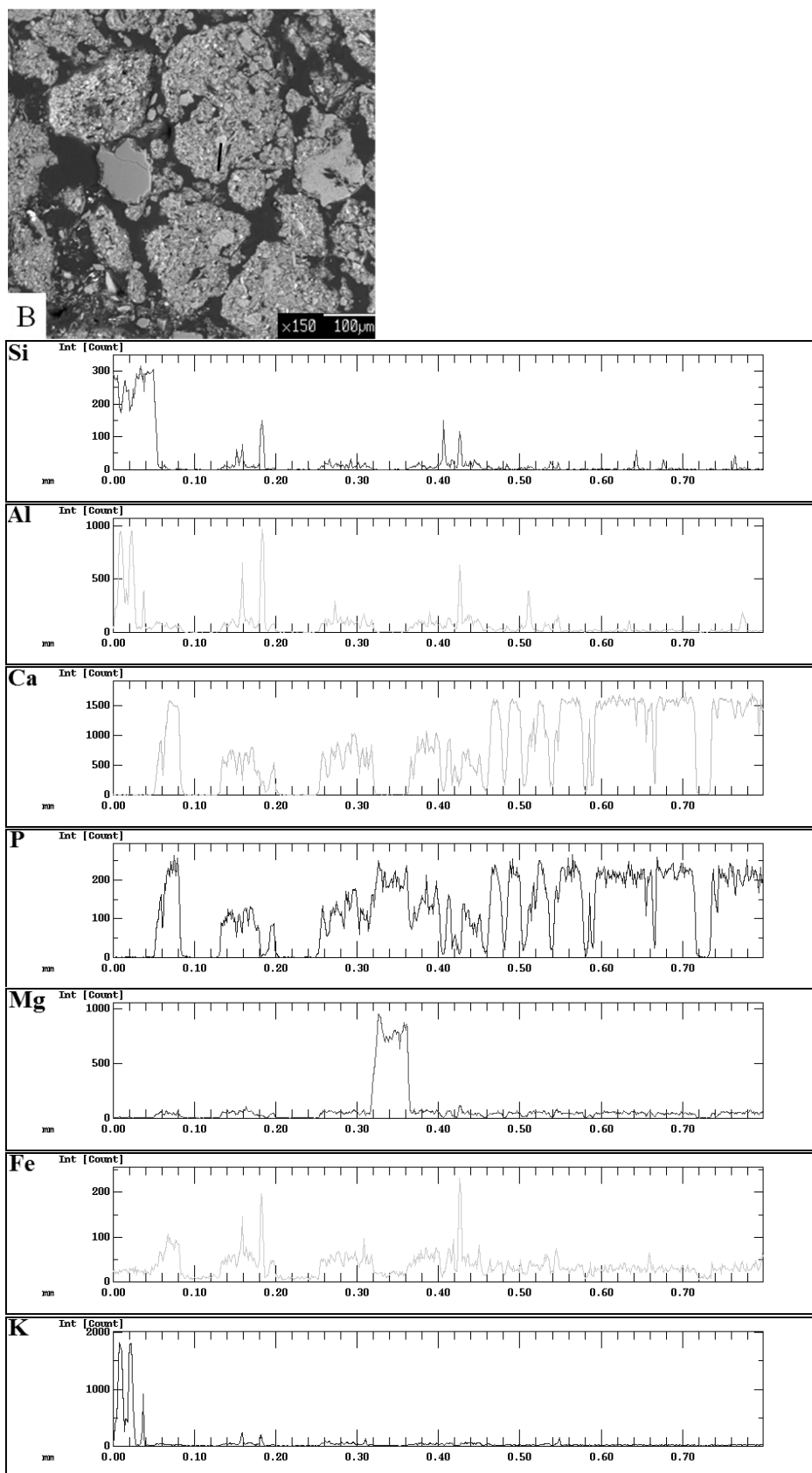


Fig. 10. Transect analysis in soil matrix with fluorapatite and struvite (pedon 17). Black line in image B show where the transect was performed.

The similar chemical composition of some features indicates the presence of discrete forms of taranakite $((K,NH_4)_3Al_5H_6(PO_4)_{8x}18H_2O)$, minyulite $(KAl_2(PO_4)_2(OH,F).4(H_2O))$, leucophosphate $((NH_4,K)_2(Fe,Al)_4(PO_4)_4(OH,F)_2 \cdot 2H_2O)$, struvite $((NH_4)MgPO_4 \cdot 6(H_2O))$, and fluorapatite $(Ca_5(PO_4)F)$ (Fig. 11), all typical of phosphatization process in ornithogenic soils (Tatur, 1989). However, P and K levels are lower than expected. Concerning the K concentration, Schaefer et al. (2008) indicate that these are degraded phases of these minerals that have lost part of K, and the lower K amounts may indicate that these minerals contain high proportions of NH_4 in their structures, since N was not analysed by WDS.

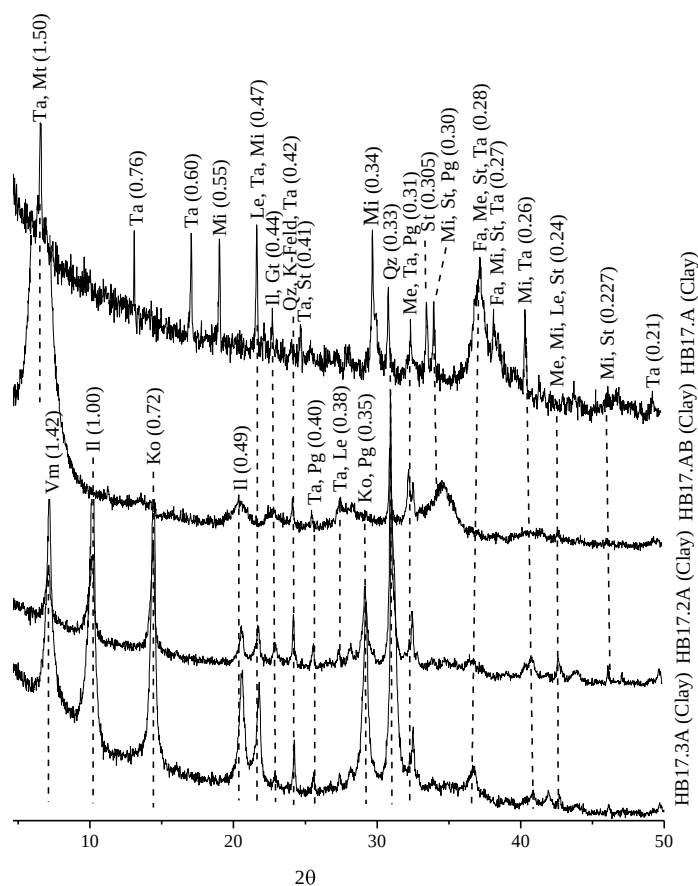


Fig. 11. XRD patterns for the ornithogenic soils of Hope Bay, Antarctic Peninsula (pedon 17). Mt – montmorillonite, Ko – kaolinite, Ta – taranakite, Le – leucophosphate, Mi – minyulite, St – struvite, Fa – fluorapatite, Me – metavariscite, Qz – quartz, K-Feld – K-feldspar, Pg – plagioclase. “d” spacing in nm.

In several pedons Al-silicates were associated with P-Fe-Mg forms, corroborating the phosphatization process. Is notorious in many pedons the affinity between P and Fe (Fig. 9), indicating P-solutions preferably reacts with Fe on the

primary mineral surfaces. These may represent very reactive amorphous Fe phases with high P adsorption capacity (Schaefer et al., 2008).

Higher levels of Fe_2O_3 were detected, whose pedofeatures were sometimes identified as $\text{Fe}(\text{OH})_3$ hydroxides. In Ornithogenic (Anthropic) Haploturbels, the contents of Fe_2O_3 associated with oxidized debris, have contributed to the peculiar phosphates forms on the mineral substrate of these sites. In pedon 15 (Table 4), a sequence of WDS analysis in Fe-oxides departing from the soil plasma to the inside of the primary mineral suggests phosphate chemical attack.

Kaolinite, detected by X-ray in the clay fraction treatments (Fig. 12), was not chemically identified WDS analysis, although some plasma compositions suggest their probable occurrence.

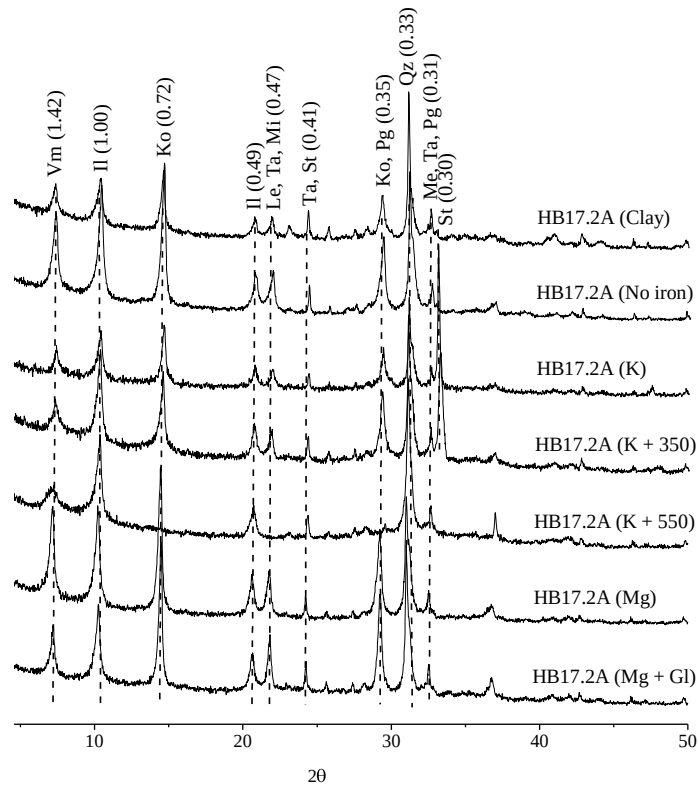


Fig. 12. XRD patterns for the ornithogenic soils at Hope Bay, Antarctic Peninsula (pedon 17 - treatments). Vm – vermiculite, Il – illite, Ta – taranakite, Le – leucophosphite, Mi – minyulite, St – struvite, Fa – fluorapatite, Me – metavariscite, Ko – kaolinite, Qz – quartz, Pg – plagioclase. “d” spacing in nm.

In pedon 14, the detection of illite, precursor of kaolinite, may help to elucidate its existence. According Tarnocai and Valentine (1989), the presence of kaolinite microaggregates in Cryosols of Canada corresponding to materials formed during warm periods, as related to the recently deglaciated areas with evidence of

higher chemical weathering, which may suggest to the formation and presence of these minerals in the clay fraction of soils of Hope Bay.

Another factor that indicates warmer conditions occurred in the past is permafrost cementation of deeper phosphate layers, during which P was leached downwards and reacted with the rock substrates.

4. CONCLUSIONS

- The soils have a moderate or strong microstructural development. A small to medium-sized granular structure is generally observed, with rounded, subrounded forms, including several well-defined ornithogenic materials, such as P-rich organic remains, nodular phosphates forms and minute fragments of bone apatite.
- The microstructure is typically orbicular, ovoidal-shaped, consistent with that is described for cryogenic fabrics of some Antarctic Cryosols. These materials are usually surrounded by secondary, concentric illuvial pedogenic P deposition.
- In the matrix, the similar chemical composition of some features indicates the presence of discrete forms of taranakite, minyulite, leucophosphite, struvite, and fluorapatite, typical of phosphatization process in ornithogenic soils. In the sand-sized fraction, plagioclases and quartz occur.
- Permafrost cementation of deeper phosphate layers indicate that warmer conditions occurred in the past, during which P was leached downwards and reacted with the rock substrates. The probable occurrence of kaolinite and goethite can be related to these conditions.
- The phosphatization process enhances chemical alteration of the substrate and is one of the main soil-forming process in ornithogenic soils.
- Chemical weathering is much more important in Maritime Antarctica, including Antarctic Peninsula, than previously thought, especially for ornithogenic soils.
- The utilization of micromorphological and microchemical techniques proved to be extremely useful for a better understanding of pedogenesis in these poorly known Antarctic soils.

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CONCLUSÕES GERAIS

- Nos sítios de monitoramento da temperatura e umidade, a neve mostrou ter grande capacidade de isolamento térmico e diferenciação microclimática. O mesmo parece estar relacionado à presença de pinguins e deposição de guano, que também resultou em diferenciações de temperatura e umidade em relação ao sítio vizinho, sem colonização atual.
- Solos de Hope Bay são geralmente distróficos, rasos, rochosos e crioturbados. Possuem pouco desenvolvimento estrutural e são pouco cromados. A ocorrência de permafrost a aproximadamente 30 cm de profundidade em toda extensão de Hope Bay reflete em forte regulação dos processos de lixiviação e desenvolvimento pedogenético. Associado à fosfatização, o permafrost parece ser a principal influência na criopedogênese envolvendo a formação dos solos locais.
- Baseado na classificação e distribuição dos solos, duas principais áreas foram separadas em Hope Bay: solos ornitogênicos nas partes baixas, até aproximadamente 60 m de altitude, e solos litólicos acima desta posição.
- A utilização de técnicas micromorfológicas e microquímicas são muito úteis para um melhor entendimento dos processos pedogéticos envolvidos em Hope Bay.