FELIPE NOGUEIRA BELLO SIMAS

SOLOS DA BAÍA DO ALMIRANTADO, ANTÁRTICA MARÍTIMA: MINERALOGIA, GÊNESE, CLASSIFICAÇÃO E BIOGEOQUÍMICA

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*"

VIÇOSA
MINAS GERAIS - BRASIL
2006

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APROVADA: 10 de abril de 2006.

Prof. Liovando Marciano da Costa
(Conselheiro)

Prof. Eduardo de Sá Mendonça
(Conselheiro)

Prof. Vander Freitas de Melo

D.S. João Herbert Moreira Viana

Prof. Carlos Ernesto G. R. Schaefer
(Orientador)

A meus pais, à minha esposa e ao Gabriel.

AGRADECIMENTOS

Primeiramente a Deus e a Virgem Mãe Criadora por tudo que se faz existente.

Aos meus pais pelo exemplo de união e alegria que me dão até hoje.

À minha esposa Ana Carolina por todo o amor e compreensão em todos os momentos, principalmente nas seguidas ausências durante o doutorado e dois natais passados na Antártica, mas, sobretudo, pelas viagens inesquecíveis que fazemos juntos!

Ao Duda e a Mariana pela união e pelo sobrinho que já vem.

Ao Carlos Ernesto por ter possibilitado meu ingresso na vida acadêmica, pelo grande professor que é e pela amizade verdadeira e força em todo o momento.

Ao compadre Pedro e à comadre Tatiana e família pelas portas abertas na vida espiritual e pela sincera amizade.

Ao Acauã, Aianã e Marcelo Mandelli pelas várias contribuições que tornaram os momentos na Antarctica mais iluminados.

A todos os irmãos e irmãs da Luz do Firmamento, da Rainha da Montanha e tantos outros Centros com os quais tenho a grande satisfação de estudar a Ciência dos saberes da floresta.

À Universidade Federal de Viçosa, por minha formação profissional.

Ao CNPq, pela concessão da bolsa.

À Marinha do Brasil, ao Ministério do Meio Ambiente e ao CNPq, pelo apoio dado durante a XXI, XXII e XXIII Operações Antárticas Brasileiras (OPERANTAR).

Aos companheiros de Antártica e de laboratório Roberto Michel, Manuel Ricardo, Marcio Francelino e Ulisses, pela amizade e ótimo convívio.

A todos os outros com quem tive a oportunidade de conviver na Antártica, em especial ao Prof. Batista e sua equipe pelo chimarrão no acampamento.

Aos grupos-base da XXI, XXII e XXIII OPERANTAR, pelo companheirismo e apoio as nossas atividades de campo.

Ao professores e funcionários do Departamento de Solos, em especial ao Prof. Liovando pelos ensinamentos e pela amizade.

À Claudinha, pelo carinho e por estar sempre lá pra nos ajudar.

Aos estagiários do CRIOSSOLOS, Vitor, Marcelo, Mariana Juliana, Isabela, Vando e Aline, pelo enorme auxílio sem o qual este trabalho não seria possível.

Ao Prof. Bob Gilkes, ao Prof. Charter Mathison e ao *staff* da *School of Earth and Geographical Sciences* e do *Centre for Microscopy and Microanalysis* da *University of Western Austrália.*

Ao Prof. Vander Freitas de Melo pela amizade e pela valorosa contribuição científica em relação ao estudo dos minerais dos solos da Antártica e a toda a sua equipe na Universidade Federal do Paraná pelas diversas análises por eles realizadas.

A outros que por descuido não tenham sido citados, mas que, de diferentes formas, contribuíram para a concretização deste trabalho.

BIOGRAFIA

FELIPE NOGUEIRA BELLO SIMAS, filho de José Roberto Bello Simas e Eliane Nogueira Bello Simas, é natural da cidade do Rio de Janeiro. Iniciou o curso de agronomia na Universidade Federal de Viçosa em 1995, graduando-se em 2000. Em 2002, obteve o título de Mestre em Solos e Nutrição de Plantas pela mesma instituição. Neste mesmo ano, ingressou no curso de Doutorado no mesmo programa de pós-graduação, submetendo-se a defesa de tese em Abril de 2006.

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APRESENTAÇÃO

Devido ao grande isolamento geográfico e as condições climáticas extremas o continente antártico é o mais intocado e menos estudado do planeta. Em 1975, o Brasil aderiu ao Tratado da Antártica, dando início ao Programa Antártico Brasileiro (PROANTAR). Desde 1982, são realizadas expedições científicas brasileiras ao continente gelado. Em 1984, foram implantados os primeiros módulos da Estação Científica Comandante Ferraz, na Baía do Almirantado, Ilha Rei George.

Em 2002, foi criada uma rede de pesquisa dentro do Programa Antártico Brasileiro (Rede 2 /PROANTAR) com objetivo de gerar subsídios para avaliar e monitorar os impactos ambientais na Baía do Almirantado. Os resultados apresentados neste trabalho são parte do Projeto Criossolos, coordenado pelo Prof. Carlos Ernesto Schaefer do Departamento de Solos da Universidade Federal de Viçosa, envolvendo diversos professores, pesquisadores, estudantes de pós-graduação e graduandos de diferentes instituições de ensino e pesquisa no país.

RESUMO

SIMAS, Felipe Nogueira Bello, D. S. Universidade Federal de Viçosa, abril de 2006. **Solos da Baía do Almirantado, Antártica Marítima: Mineralogia, Gênese, Classificação e Biogeoquímica.** Orientador: Carlos Ernesto Gonçalves Reynaud Schaefer. Conselheiros: Liovando Marciano da Costa e Eduardo de Sá Mendonça.

A maioria dos estudos pedológicos na Antártica foram realizados na porção oriental do continente, onde as constantes temperaturas negativas restringem a presença de água no estado líquido. Nestes “desertos gelados”, a formação dos solos se dá através de processos de intemperismo físico, com elevado acúmulo de sais solúveis nos solos. Por outro lado, na região da Antártica Marítima, temperaturas mais elevadas e maiores precipitações permitem uma maior participação de processo químicos e biológicos na formação dos solos e ecossistemas terrestres. O presente trabalho objetivou a caracterização química, física, mineralógica e micromorfológica dos principais solos da Baía do Almirantado, Ilha Rei George. Foram descritos e amostrados mais de 60 perfis. Os solos foram submetidos a análises químicas e físicas de rotina e estudados a partir de extrações químicas seqüenciais, difração de raios-X (DRX), microscopia eletrônica de varredura e de transmissão e microanálises. Avaliou-se o estoque de C orgânico e a distribuição das frações húmicas nos solos assim como a bioacumulação de metais pesados e outros elementos pela vegetação antártica. Os solos estudados caracterizam-se pela presença de *permafrost* (camada de solo permanentemente congelada), sendo classificados como Cryosols ou Gelisols pelos sistemas de classificação da FAO (WRB) e Soil Taxonomy, respectivamente. De maneira geral os solos apresentam maior desenvolvimento do que aqueles descritos para porções mais frias e secas da Antártica. São solos com desenvolvimento incipiente, com intensa ação do intemperismo físico e características químicas estreitamente relacionadas ao material de origem. Foram identificados os seguintes tipos de solos na Baía do Almirantado: a) solos derivados de basaltos e andesitos; b) solos tiomórficos formados a partir de andesitos priritzados; c) solos ornitogênicos (formados sob influência de dejetos de aves). A fração argila dos solos basálticos/andesíticos é composta principalmente por esmectita interstratificada com esmectica com hidroxi-Al entre camadas. Nos solos tiomórficos, caulinita, clorita e um mineral interstratificado illita-esmectita foram detectados. Nestes solos, a oxidação de sulfetos promove intensa acidificação, com formação de jarosita e minerais amorfos de Fe. Fosfatos cristalinos de Al e Fe constituem grande parte da fração argila de solos ornitogênicos. Fosfatos amorfos contendo Al, Si e Fe controlam as características químicas nestes ambientes. Do ponto de vista micromorfológico, os solos apresentam feições típicas de solos criogênicos, nos quais os ciclos de congelamento e descongelamento favorecem a formação de estruturas granulares altamente estáveis. Análises microquímicas permitiram o detalhamento dos processos de oxidação de sulfetos e de fosfatização. Ao contrário dos solos da Antártica continental, o intemperismo químico é ativo nos solos da Baía do Almirantado, especialmente nos pedoambientes onde ocorre a oxidação de sulfetos ou intensa atividade de aves. Nestas últimas há o desenvolvimento de extensas coberturas vegetais com ocorrência das duas únicas plantas superiores que ocorrem na Antártica (*Deschampsia antarctica* Desv. (Poaceae) e *Colobanthus quitensis* (Kunth) Bartl. (Caryophillaceae)). Os teores de C orgânico nos solos são mais elevados, com formação de espessos horizontesl híticos. Solos mais desenvolvidos apresentam maior participação das frações ácido fúlvico e húmico. Os níveis de metais pesados em todas as espécies vegetais estudadas foram muito baixos.

ABSTRACT

SIMAS, Felipe Nogueira Bello, D. S. Universidade Federal de Viçosa, April 2006. **Soils from Admiralty Bay, Maritime Antarctica: Mineralogy, Genesis, Classification and Biogeochemistry.** Adviser: Carlos Ernesto Gonçalves Reynaud Schaefer. Committee Members: Liovando Marciano da Costa and Eduardo de Sá Mendonça.

Soils from Maritime Antarctica are less studied than that from colder and dryer zones of Antarctica. In this work, we present analytical and morphological data for the main soil types found in Admiralty Bay, King George Island. The soils were classified according to the Soil Taxonomy and WRB systems and analyzed according to standard international soil characterization methods. X-ray diffraction, differential thermal and thermogravimetric analysis, scanning and transmission electron microscopy, energy dispersive spectrometry and selective chemical dissolution were used to characterize clay fraction mineralogy and soils micromorphological aspects. Soils organic C stocks were estimated as well as the distribution of humic substances for the different soil types. The bioaccumulation of heavy metals and other elements in species of lichens, mosses and higher plants was studied. Randomly interestratified smectite-hydroxi-Al interlayered smectite is the main clay mineral in basaltic/andesitic soils. Kaolinite, chlorite, regularly interstratified illite-smectite, jarosite and amorphous Fe phases are present in acid sulphate soils. Crystalline Al and Fe phosphates occur at sites directly affected by penguins. Highly reactive non-crystalline Al, Si, Fe and P phases control soils chemical characteristics at ornithogenic sites. Chemical weathering is an active process in Cryosols from Maritime Antarctica and is enhanced by the oxidation of sulphides for some parent materials and by faunal activity. The microfabrics of the studied soils are strongly influenced by the lithological fabric with high proportions of primary minerals in all fractions. The sub-angular characteristics of sand-sized and coarser particles indicate short-distance transport. The increasing roundness of lithorelicts with decreasing particle size reflects the effects of differential frost heaving and intense cryoturbation. Chemical weathering is much more important in Maritime Antarctica than previously thought, especially for acid sulphate and ornithogenic soils. The use of micromorphological and microchemical techniques proved to be extremely useful for a better understanding of pedogenesis in these poorly studied environments. Despite their reduced geographic expression, ornithogenic soils are without doubts the most important compartment of immobilized organic C in ice-free areas of Admiralty Bay. The presence of higher plants at these sites coincides with high organic C levels with depth. At poorly drained sites, accumulation of moss remains originated deep, fibric, organic soils with considerable levels of organic C in the permafrost layer. Eventual global warming and permafrost degradation may increase C emissions at these sites. The levels of Cd, As, Cr, Ni and Pb in the plants studied in this work were lower than that reported for other remote areas of the world and suggest negligible contamination for the terrestrial ecosystems of Admiralty Bay.

INTRODUÇÃO GERAL

Os ecossistemas terrestres da Antárctica restringem-se a áreas livres de gelo distribuídas ao longo da costa ou em cadeias montanhosas, representando cerca de 2% da área total do continente (Campbell and Claridge, 1987). A maior parte dos estudos pedológicos foram realizados na Antarctica oriental onde temperaturas negativas constantes restringem a presença de água líquida, condicionando um sistema desértico (deserto gelado). Nestes ambientes, a formação de solos se dá através de processos físicos de intemperismo, com elevado acúmulo de sais solúveis.

A Antártica Marítima engloba a costa oeste da Península Antártica, ao norte do paralelo 70º S, e os arquipélagos das Sandwich e Shetlands do Sul. Esta é a porção mais quente e úmida da Antártica, na qual os solos permanecem descongelados por praticamente 3 meses por ano. As condições climáticas (temperaturas mais elevadas e maior precipitação) favorecem a atividade biológica, com o desenvolvimento de algas, liquens e extensos tapetes de musgos. As duas únicas plantas superiores que ocorrem na Antártica (*Deschampsia antarctica* Desv. (Poaceae) e *Colobanthus quitensis* (Kunth) Bartl. (Caryophyllaceae)) estão restritas à Antártica Marítima.

Grande parte dos estudos de solos nesta porção da Antártica trata principalmente de solos afetados pela atividade de aves. A cada ano, a intensa utilização do ambiente terrestre pela avifauna, em especial por pingüins, resulta no elevado aporte de material orgânico e nutrientes, especialmente P e N. A interação do guano com o substrato mineral resulta na formação de minerais de fosfato raramente encontrados em ambientes naturais.

Os solos antárticos são de grande interesse científico, pois representam o resultado da interação de fatores de formação do solo em condições únicas no planeta. O entendimento dos processos de intemperismo químico e físico na formação/transformação de minerais e da dinâmica biogeoquímica nestas condições extremas é de grande relevância não só para o entendimento do ecossistema Antárctico, mas também para a melhor compreensão da formação de solos em outras regiões do planeta.

O objetivo geral do presente trabalho foi estudar em detalhe os solos da Baía do Almirantado, Ilha Rei George, a fim de contribuir para uma maior compreensão dos ecossistemas terrestres da Antártica Marítima e gerar bases para o gerenciamento ambiental da região. Para tanto, foram realizados diversos procedimentos visando:

- Estudar a gênese e os principais atributos químicos, físicos e morfológicos dos solos da Baía do Almirantado.
- Classificar os solos de acordo com os sistemas FAO-UNESCO (WRB) e Soil Taxonomy e sugerir eventuais alterações nestes sistemas para uma melhor classificação dos solos da Antártica.
- Avaliar os impactos da atividade da avifauna e do processo de *fosfatização* na formação dos solos e comunidades vegetais na área de estudo.
- Caracterizar através de técnicas avançadas de microscopia eletrônica a mineralogia da fração argila e as características micromorfológicas dos principais solos da Baía do Almirantado.
- Estimar o estoque de carbono orgânico e estudar a distribuição das frações húmicas em diferentes solos nas áreas livres de gelo da Baía do Almirantado.
- Estudar os teores de metais pesados e outros elementos em musgos, líquens e plantas superiores de diferentes partes da Baía do Almirantado.

CAPÍTULO 1

Genesis, properties and classification of Cryosols from Admiralty Bay, Maritime Antarctica

Abstract

Soils from Maritime Antarctica are distinctly different than that from other climatic zones and are the least studied soils in Antarctica. In this work we present analytical and morphological data for the main soil types found in Admiralty Bay, King George Island. Fifty-six (56) pedons were dug, collected and analyzed according to standard international soil characterization methods and were classified according to the Soil Taxonomy and WRB systems. Soils are generally poorly developed and have chemical, physical and morphological characteristic strongly influenced by the parent material. We identified four main soil types: (i) Basaltic/andesitic, (ii) acid sulphate, (iii) weakly ornithogenic and (iv) ornithogenic soils. Small changes were proposed for both classification systems to allow a more adequate classification for some of the studied soils. Greyish colored, eutric Lithic and Typic Haploturbels (Thurbi-leptic Cryosols) with neutral to alkaline reaction are the most common soils and are usually developed from basaltic/andesitic till. Yellowish, acid, dystric Sulphuric Haploturbels (Turbi-thionic Cryosols) are restricted to areas affected by pyritized andesite, found mainly in Keller Peninsula and Crépin Point. Umbriturbels (Turbi-umbric Cryosols) only occur at sites under bird influence. Ornithogenic soils are the most developed soils in Admiralty Bay with pronounced chemical, physical and morphological alteration of parent materials due to past and currente penguin activity, with formation of umbric epipedons and phosphatic B horizons. Organic Fibristels (Organo-turbic Cryosols) are restricted to hydromorphic areas under exuberant moss carpets.

Key words: Cryosols, permafrost, Maritime Antarctica, ornithogenesis, pedogenesis, soils

1. Introduction

Soil formation in Antarctica is restricted to less than 2 % of the continent, comprising ice-free areas located around the coast and dry glacial valleys along mountain ranges (Campbell and Claridge, 1987, Bockheim, 1997; Bockheim and Tarnocai, 1998). Most pedological knowledge for Antarctica comes from permanently frozen, desert ice-free areas where soils are poorly developed and show appreciable accumulation of water-soluble salts (Campbell and Claridge, 1987; Bockheim, 1997; Bockheim and Tarnocai, 1998; Campbell and Claridge, 2004a, b). Relatively little information is available on genesis and classification of soils from Maritime Antarctica in relation to their continental counterparts (Tatur, 1989; Blume et al., 2004; Schaefer et al., 2004; Albuquerque-Filho, 2005; Michel et al., 2006).

It is known that soils from Maritime Antarctica are distinctly different than that from other climatic zones (Campbell and Claridge, 1987; Blume et al., 2004; Michel et al., 2006). Warmer temperatures and higher water availability result in deeper active layers and favor primary production and mineral weathering (Campbell and Claridge, 1987; Blume et al., 2004). Strong influence by sea birds enhances biodiversity and nutrient availability in some sites leading to the formation of the so-called ornithogenic soils (Ugollini 1970; Ugollini 1972; Tatur, 1989; Tatur et al., 1997). Despite the increasing number of studies during the last 10 years (Tatur, 1989; Tatur et al., 1997; Blume et al., 2002, 2004; Goryachkin et al., 2004; Albuquerque-Filho, 2005), Maritime Antarctica is still one of the least studied parts of Antarctica in terms of soils and permafrost.

From 2002 to 2005, a detailed soil survey was carried out in Admiralty Bay, Maritime Antarctica as part of the Brazilian Antarctic Research Program. The objectives of the present work are: (1) to present analytical and morphological data for the main soil types found in Admiralty Bay; (2) discuss the processes and factors which govern soil formation in this part of Antarctica and; (3) classify the soils of according to the WRB and Soil Taxonomy classification systems.

2. Material and Methods

The Admiralty Bay (62°03’40”-62°05’40” S and 58°23’30”-58°24’30” W) is located in King George Island and is part of the South Shetlands Archipelago, Maritime Antartica (Figure 1). Data sets from 1982-2002 acquired at the Brazilian Comandante Ferraz Station, report mean air temperatures varying from -6.4 ^{o}C in July to +2.3 ^{o}C in February. Mean annual precipitation is 366.7 mm. Positive air temperatures occur from November until March when effective precipitation as liquid water is increased due to melting of accumulated winter snow. Soils have formed predominantly from tholeite basalts and, to a lesser extent, from sulphide-bearing andesites and related moraine, solifluction and fluvioglacial deposits. Several data indicates that deglaciation at King George Island occurred ~ 6000 years ago and a climatic optimum occurred between ca. 4000 and 3000 years ago (Bjorck et al., 1991; Yoon et al., 2000). Occasional deposition of volcanic ash has also been reported (Blume et al., 2004; Jeong and Yoon, 2001).

Fifty six (56) pedons distributed in the major ice-free areas of Admiralty Bay were sampled and analyzed (Figure 1 and Table 1). Soils were sampled in 10 cm layers but horizon boundaries were respected. Soil classifications followed the Soil Taxonomy (SSSA, 2003) and the *World Reference Base for Soil Resources* (WRB) classification systems (ISSS, 1998). For the latter, the recommendations by Tarnocai et al., (2004) were considered.

Soil pH, exchangeable nutrients and texture were determined for < 2 mm air-dried samples (EMBRAPA, 1997). Exchangeable Ca^{+2}, Mg^{+2} and Al^{+3} were extracted with 1 mol/L KCl and P, Na and K with Melich-1 (EMBRAPA, 1997). Nutrient levels in the extracts were determined by atomic absorption (Ca^{+2}, Mg^{+2} and Al^{+3}), flame emission (K and Na) and photocolorimetry (P). Total organic C was determined on < 0.5 mm samples by wet combustion (Yeomans and Breemen, 1988). Total nitrogen was determined by the Kjeldahl method (EMBRAPA, 1997). Soil texture was obtained through mechanical dispersion of < 2 mm samples in distilled water, sieving and weighing of coarse and fine sand, sedimentation of silt followed by siphoning of the < 2 µm fraction (Gee and Bauder, 1986). Clay fraction mineralogy for selected pedons was studied in detail using chemical dissolution, X-ray diffracttion (XRD) and electronic microscopy (Chapter 3).

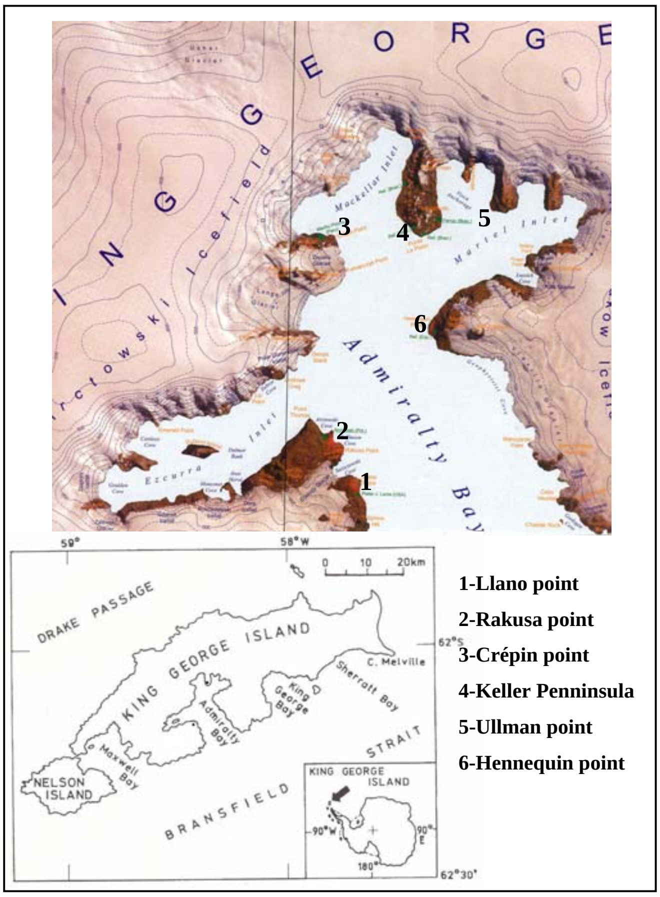

Figure 1 – Localization of Admiralty Bay in King George Island, north of the Antarctic Peninsula. Numbers 1-6 indicate the ice-free areas sampled for this study.

Table1 – Number of pedons studied in the main ice-free areas at Admiralty Bay.

Location	No. of Pedons
Keller Peninsula	25
Crépin point	4
Rakusa point	10
Llano point	10
Hennequin point	3
Ullman point	4

3. Results and Discussion

3.1 General characteristics

All soils that we studied in Admiralty Bay had permafrost in the upper 100 cm and therefore fit in the Gelisol order and in the Cryosol major group according to the Soil Taxonomy (SSSA, 2003) and the *World Reference Base for Soil Resources* (ISSS, 1998), respectively. Typical cryoturbation features (Bockheim and Tarnocai, 1998; Tarnocai et al., 2004) such as patterned ground (i.e. stone circles, stripes and earth hummocks), irregular and broken horizons, vertical orientation of stones within the soil profile, buried organic matter and formation of silt caps are commonly observed. High proportions of > 2 mm particles (including large rock fragments) result in a sandy-skeletal texture for the bulk soils and a primary single grain structure. However, the entrapment of sand fragments by silt and clay forming rounded aggregates also occurs resulting in medium sized granules. At midsummer, most soils presented permafrost starting from 40 to 60 cm from the soil surface.

Based on their physical, chemical, mineralogical and morphological characteristics the soils from Admiralty Bay were grouped in: i) Basalt/andesitic soils; ii) Acid sulphate soils; (iii) Soils under weak ornithogenic influence and; iv) Ornithogenic soils. Some geographical, morphological, mineralogical, chemical and physical characteristics for each soil group are summarized in Tables 2 and 3. Figure 2 shows representative pedons for each soil group and detailed descriptions for representative pedons are presented in Table 4.

Table 2 – Geographic distribution, clay fraction mineralogy, color, structure and degree of horizon differentiation for the main soil groups in Admiralty Bay.

Soil Group	Occurrence	Clay fraction mineralogy[1]	Dry Color	Structure	Horizon formation
Basalt/andesitic soils	All ice free areas	HIS-sme > pyr, pl, > all	Grey (2,5Y 6/2) greyish brown (10YR 5/2)	Single grain; weak, medium granular	Poorly defined; incipient A horizon at vegetated sites.
Acid sulphate	Keller Peninsula and Crépin Point	ka, ch, I-S > ja > feh	Pale yellow Yellow (2,5Y 7/6)	Single grain; moderate, medium granular	Formation of A horizon
Weakly Ornithogenic	All ice free areas specially Hennequin Point and the western coast of Admiralty Bay	HIS-sme > pyr, pl, > all	Brown (10YR 4/3)	Single grain; Moderate, medium granular; Crumbs	Clear A horizon; umbric epipedon
Ornithogenic	Western coast: Llano and Rakusa point	A.P. > C.P. > HIS-sme	Yellowish brown (10YR 5/4) Light grey (2,5Y 7/2) Dark brown (7,5YR 7/4)	Single grain; strong granular; weak blocks; Crumbs.	Clear O and A horizons; formation "phosphatized" cambic B horizons

[1] data presented in Chapter 3. HIS-sme – interstratified smectite-hydroxi-interlayered-smectite; pyr – pyroxene; pl - plagioclase; all – allophane; ka - kaolinite; ch – chlorite; I-S – interstratified illite-smectite; ja – jarosite; feh – ferrihydrite; A.P – amorphous organic matter-bound phosphates; C.P - crystalline phosphates (leucophosphite, minyulite, variscite).

Table 3 – Mean and standard deviation of some chemical and physical properties for the main soil types from Admiraly Bay.

Soil type	^{1}n	pH	^{2}P	^{2}K	^{2}Na	^{3}Ca^{2+}	^{3}Mg^{2+}	^{3}Al^{3+}	^{4}COT	^{4}N	> 2 mm	sand	silt	clay
		H_2O	----------------mg/dm--------------^{3}			-----------cmol$_c$/dm^3----------			-------g/kg------		------------------------------g/kg----------------------------			
Basaltic/ andesitic	86	7.4 ± 0.6	266.4 ± 163.6	83.5 ± 45.0	225.8 ± 242.4	24.6 ±15.5	7.2 ±11.6	0.06 ± 0.2	3.5 ± 5.1	n.d.	300- 860	380 ± 160	320 ±70	250 ± 50
Acid sulphate	16	4.9 ± 0.5	39.7 ± 25.8	55.2 ± 32.8	117.2 ± 47.4	10.1 ± 6.1	5.0 ± 4.5	14.5 ± 13.4	5.0 ± 8.4	n.d.	90 – 680	410 ± 230	450 ± 190	58 ± 51
Weakly ornithogenic	73	6.3 ± 0.8	252.4 ± 151.8	291.8 ± 258.8	202.9 ± 104.5	13.1 ± 7.3	6.4 ± 5.6	1.4 ± 3.4	12.2 ± 12.8	2.7 ± 3.0	160 – 730	410 ± 180	320 ±40	210 ± 80
Ornithogenic soils	41	4.1 ± 0.3	1356.7 ± 956..3	856.6 ± 293.6	372.0 ± 254.7	4.7 ± 5.6	1.5 ± 2.5	7.1 ± 3.4	32.0 ± 29.0	4.3 ± 1.0	180 - 950	730 ± 100	150 ± 70	110 ± 40

[1] number of analyzed samples for each soil group; [2] extracted with Melich-1; [3] exchangeable Ca^{2+}, Mg^{2+} and Al^{3+}; [4] total organic C and total N.

Figure 2– Photographs illustrating representative pedons for each main soil group found at Admiralty Bay. **Basaltic/andesitic soils:** A) Pedon K17, Typic Haploturbel from subpolar desert ladscape; B) Pedon K6, Typic Aquiturbel from marine terrace. **Acid Sulphate Soils:** C) Pedon K24, Sulphuric Haploturbel with typical yellow color. **Weakly Ornithogenic soils:** D) Pedon K23, Leptic Haploturbel under weak ornithogenic influence and well developed A horizon. **Ornithogenic Soils:** E) Pedon A3, Ornithogenic Psammoturbel with whitish phosphatic horizon mixed by cryoturbation with material from the A horizon; F) Pedon C3, Ornithogenic Umbriturbel adjacent to penguin rookeries at Llano Point.

Table 4 – Morphological and analytical data for representative pedons of each soil group

Pedon[1]	Location	Parent Material	Hor	Depth (cm)	Color (dry)	> 2 mm %	Texture (< 2mm) %	Structure[2]	pH	TOC g/kg	Comments
						Basaltic/andesitic soils					
K17- TH	Keller (Tyrrel Plateau)	Basaltic and andesitic till	C1	0-10	2,5Y 5/3	42	Clay loam	sg, mg	7.7	1.0	Well-drained cryoplanation surface at approximately 200 m above sea level (m.a.s.l.) No vegetation cover.
			C2	10-35	2,5Y 6/3	-	Clay loam	sg, mg	7.8	1.0	
			C3	35-60	2,5Y 5/2	59	Clay loam	sg, mg	7.3	1.0	
K6-LA	Keller	Fluviomarine sediments	A	0-10	2,5Y 4/2	79	Sandy clay loam	sg, m	7.9	5.0	uplifted marine terrace at approximately 5 m a.s.l. with exuberant continuous moss cover. Poorly drained
			C	10-40	2,5Y 5/4	53	Sandy clay loam	sg, m	7.9	2.0	
						Acid sulphate soils					
K24-SH	Keller (west coast)	Pyritized Andesite	AC	0-20	2,5Y 5/4	58	Sandy loam	sg, mg	5.0	5.0	stable moraine composed of oxidized sulphide-bearing till at 47 m.a.s.l. Well-drained, with high gravel content as sparse vegetation cover of mosses, lichens and rare *Deschampsia sp.*
			C	20-60	2,5Y 7/6	38	Silt loam	sg	4.4	1.0	
						Weakly ornithogenic soils					
K23-LH	Keller	Basaltic till	A/D	0-10	10YR 4/3	70	Loamy sand	sg, mg	5.3	36.4	Well-drained soil at 100 m.a.s.l. Influence of Skuas. Well-developed vegetation covering a desert pavement composed of angular fragments.
			AC	10-50	2,5Y 5/4	16	Loamy sand	sg	6.2	15.0	
						Ornithogenic soils					
A3-OP	Rakusa Point	Basaltic till	A1	0-8	10YR 5/3	49	Sand	sg, cr	4.6	15.0	probable highest level of previous penguin occupation at 69 m.a.s.l. Abundant phosphatization and well developed vegetation cover with higher plants. Abundant fine roots in the A horizon.
			A2	8-20	10YR 5/3	-	Sand	sg,	4.3	8.0	
			BC	20-40	10YR 6/4	51	Sand	sg	4.0	14.0	
			C	40-60	10YR 6/3	-	Sand	-	4.0	13.0	
C2 – LU	Llano Point	Andesitic till	O	0-10	10YR 3/2	-	-	-	4.8	86.0	poorly drained area adjacent to penguin rookery at 30 m a.s.l. Thick moss carpet.
			A	10-25	10YR 4/2	-	Sandy-loam	sg, wb,	4.5	48.0	
			CR	25-60	7,5YR 3/3	-	Sandy-loam	sg	4.2	77.0	
A7- OF	Rakusa Point	Basaltic till and poorly decomposed moss fibers	O1	0-20	10YR 4/4	31	Loamy-sand	-	4.3	69.0	Moss peat preserved from erosion by a basaltic dyke. High volume of fibric organic material.
			O2	20-40	10YR 4/4	18	Loamy-sand	wb, cr	4.2	134.0	
			O3	40-90	10 YR 4/4	18	Loamy-sand	m	4.2	95.0	

[1] TH – Typic Haploturbel; SH – Sulphuric Haploturbel; LH – Lithic Haploturbel; LA – Lithic Aquiturbel; OP – Ornithogenic Psammoturbel; LU – Lithic Umbriturbel; OF – Ornithogenic Fibristel; [2] sg- single grain; mg – medium granular; m-massive; wb – weak blocks; cr- crumbs

3.2 Basaltic/andesitic soils

Intense cryoturbation and reworking of till in ice-free areas of Admiralty Bay results in the mixture of basaltic and andesitic materials. Although in some areas soils are formed *in situ* most soils form from mixtures of different volcanic rocks (Figure 2-A). Soil morphology reflects the nature of the till, with darker soils in more basaltic areas and grayish-greenish soils in predominantly andesitic areas. At the uppermost part of the landscape soils are practically devoid of vegetation cover (Figure 3) except for sparse epilithic lichens. Soils present high pH, Na and especially Ca levels (Table 3). The levels of organic C and total N are very low (Table 3) and soils have virtually no clear horizon differentiation (Figure 2 A, Table 4).

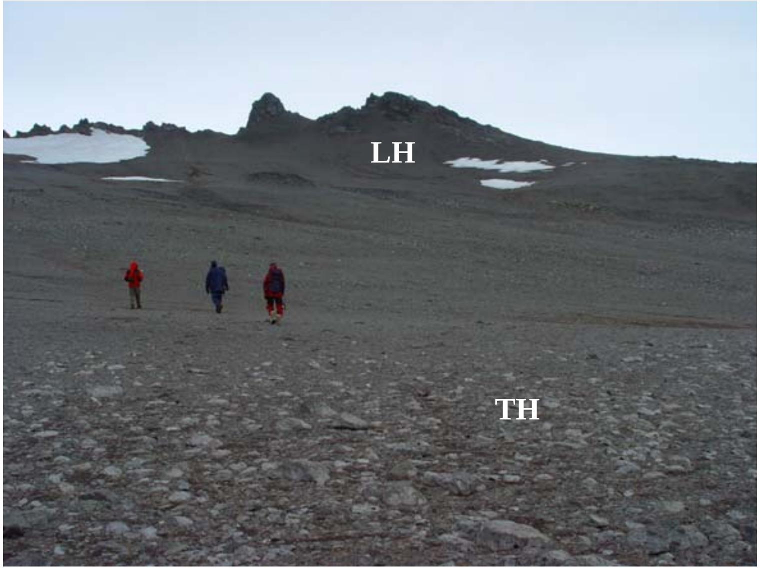

Figure 3 – Subpolar desert landscape formed from basaltic /andesitc materials. Typic Haploturbels (TH) are found in valley floors while Lithic Haploturbels (LH) dominate the uppermost areas.

At more humid sites, cryptogamic organisms (mosses and lichens) form continuous covers (Figure 4-A) and A horizons are formed (Figure 4-B). A sharp boundary is observed between the fibric A or O horizon and the underlying mineral horizon (Figure 4-B) with abrupt reduction of organic C levels with depth (Table 4 – pedon K6). Soils from stable moraines and marine terraces have their deepest layers frequently saturated with water and form gleyed horizons (Figure 2-B). At some marine terraces, sandy soils present large rounded stones which are covered by a reddish iron precipitate evidencing lateral migration of Fe^{2+} from upslope with precipitation of Fe^{3+} at more oxidizing pedoenvironments (Figure 5).

Soils have relatively high amounts of (clay + silt) (Table 3) in comparison to soils from the Cold Desert (Bockheim, 1997). A weak medium-sized granular structure composed of concentric deposition of fines around coarser fragments is typical of well-drained horizons, whereas in saturated horizons a massive structure is usually present. The formation of granular structure in Cryosols is attributed to differential freeze-and-thawing and ultradissecation of soil fine particles during the freezing process (Van Vliet Lanoe., 2004).

We have detected the presence of weatherable primary minerals such as pyroxenes and plagioclase in the clay fraction of well-drained, desert basaltic/andesitc soils indicating that chemical weathering is slow (Chapter 3). The dominantly smectitic clay fraction mineralogy has been attributed to cryoclastic particle-size reduction of hydrothermally altered rock minerals (Jeong and Yooon, 2001; Chapter 3). Nevertheless, the formation of pedogenic iron oxides (Blume et al., 2002; Chapters 2 and 3), hydroxi-interlayered-smectites and the detection of up to 20 % of allophane-like minerals in the clay fraction for these soils suggests that chemical weathering is occurring (Chapter 3). The soils from this group fit in one of the following classes: Typic, Lithic or Aquic Haploturbels (SSSA, 2003) which are equivalent to Turbi-leptic, Turbi-lithic and Turbi-stagnic Cryosols (Tarnocai et al., 2004). Andic properties were not commonly observed in the studied area.

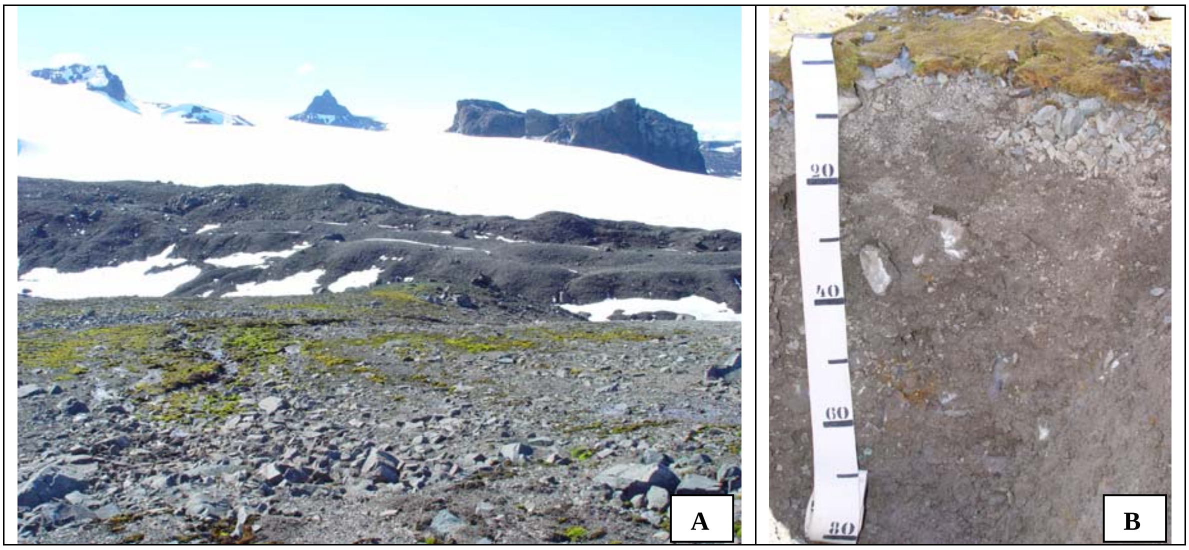

Figure 4 – Humid basaltic/andesitic moraines with cryptogamic vegetation (A) and formation of incipient A horizon (B).

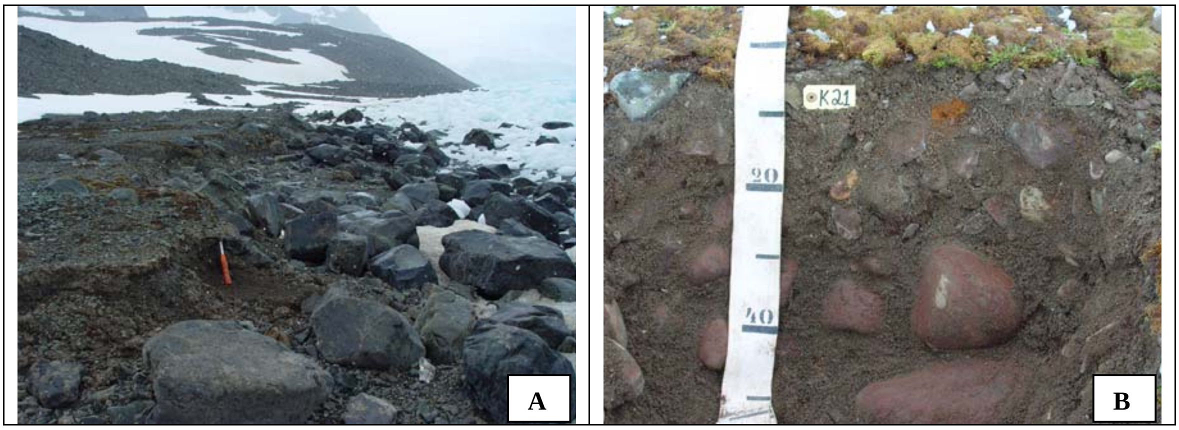

Figure 5 –Lithic Haploturbel from basaltic/andesitic marine terrace. Abundant reddish varnish on the rock surfaces indicates lateral migration of reduced iron and precipitation of Fe^{3+}.

3.3 Acid sulphate soils

These soils have formed from sulphide bearing andesites and related till (Figure 6) which occur mainly in Keller Peninsula and Crépin Point. They are normally well-drained with clear cryoturbation features and have characteristic yellow colors and stable granular structure (Table 2, Figure 3-B). The oxidation of sulphides has promoted soils acidification (Table 2 and Table 3 - pedon K24) with formation of secondary sulphates (jarosite and natrojarosite), ferrihydrite and sulphuric horizons (see Chapter 3 in this thesis). The presence of kaolinite reported for these soils indicates chemical weathering of primary minerals (Chapter 3) The low mean soil pH favors the flocculation of fine particles and formation of stable silt-sized rounded aggregates. In order to avoid alteration of soils natural characteristics and possible mineral transformations, no dispersant was used in the textural analysis resulting in very low clay levels for these soils (Table 3). However, clay + silt values are relatively high indicating that part of the clay fraction is present as silt sized aggregates.

Figure 6 – Outcrops of oxidized sulphide-bearing andesites (yellowish colors) at the eastern coast of Keller Peninsula (left) and large acid moraine (right) on which Sulphuric Haploturbels are formed.

According to the WRB system, these soils were classified as Turbi-thionic Cryosols (Tarnocai et al., 2004). However, within the Soil Taxonomy the *sulphuric* qualifier is only applicable for Aquiturbels which is definitely not the case for these well-drained, oxidized soils. Therefore we propose the inclusion of the *Sulphuric* Haploturbel to classify well drained cryoturbated soils with sulphuric materials in the upper 100 cm.

3.4 Soils with weak ornithogenic influence

These soils are formed in both basaltic and acid sulphate substrates due to the influence of flying birds, such as skuas, giant petrels and sea-gulls (Figure 7). They occur in all ice-free areas normally as discontinuous patches of exuberant vegetation composed by lichens, mosses and flowering plants. At Hennequin Point (eastern coast of Admiralty Bay), uplifted marine terraces are used annually by skuas for nesting and reproduction, representing one of the largest continuous units of these soils in Admiralty Bay. At the western coast, numerous nests are localized around penguin rookeries since most of the above mentioned flying birds prey on penguins.

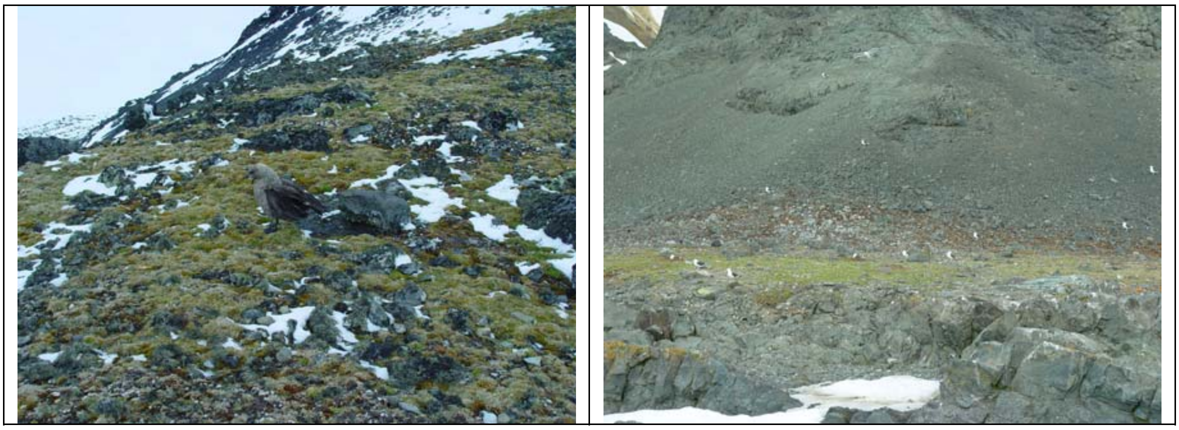

Figure 7 - Nesting areas of skuas (left) and seagulls (right).

Well-developed A horizons are typical in these soils (Figure 2-D). The chemical and morphological characteristics of the original parent material are altered with formation of dark brown surface horizons (Table 2). Basaltic/andesitic materials are acidified and depleted in Na and Ca while organic C and total N levels are increased (Table 3, Table 4 – pedon K23). At more stable and well-drained sites, with a longer history of bird occupation, the formation of umbric epipedons with a more developed structure occurs. There, carbon stocks are considerable and sometimes comparable to that reported for ornithogenic soils from penguin rookeries (Chapter 5). The pedons of this group were classified in one of the following classes: Lithic or Aquic Umbriturbels and Lithic Haploturbels (SSSA, 2003) which correspond to Turbi-umbric Cryosols, Turbi-stagnic Cryosols and Turbi-lithic Cryosols respectively.

3.5 Ornithogenic soils

Ornithogenic soils in Antarctica occur at active or abandoned penguin rookeries and are quite well studied (Ugolini, 1970; Ugolini, 1972; Campbell and Claridge, 1987; Tatur, 1989). In Admiralty Bay, penguin rookeries are restricted to the west coast, at Rakusa Point and Llano Point. Under the humid maritime climate, intense cryoturbation and water percolation incorporates bird detritus deep in the profile. P-rich leachates react with the mineral substrate in a complex process of soil “phosphatization”, first described by Tatur and Barczuk (1985) and studied in detail in Chapters 2 and 3 of the present thesis.

In active rookeries (Figure 8- A and B), continuous deposition of fresh guano inhibits vegetation establishment and soils are covered by layers of guano, rich in calcium phosphates and avian detritus (bones, feathers, egg shells) (Tatur, 1989; Tatur et al., 1997). In abandoned penguin rookeries, soils are covered by dense vegetation communities with higher plants (Figure 8- C and D). Ornithogenic soils are acid, normally dystric and have anomalously high total and bioavailable P levels (Table 3, Table 4 – pedons A3 and C2; see also Chapter 2). The content of fine particles (silt + clay) is usually lower than that reported for other soils from Admiralty Bay and maybe due to the attack of aluminosilicates by the high acidolysis occurring in these soils due to fresh guano microbial stabilization. Several amorphous and crystalline P-rich minerals dominate soils fine fraction below 20 cm (Tatur et al.,1997; Chapters 2 and 3).

The ornithogenic soils have a distinct morphology with formation of discrete light grey and yellowish-brown phosphatic horizons (Figure 2-E). At surface, high organic matter accumulation occurs with formation of dark brown umbric epipedons. In poorly drained areas, moss peats (Histels or Organic Cryosols) have formed and part of the organic matter is preserved in the frozen soil layers (Table 4). Despite their reduced geographical expression, these soils are important organic C reservoirs in Antarctic terrestrial ecosystems. Several authors have suggested the inclusion of the *ornithogenic* qualifier for a more adequate classification of these unique soils (Tarnocai et al., 2004; Chapter 2 in this thesis). In this work, the soils were classified as: Ornithogenic Psammoturbels, Haploturbels, Aquiturbels and Fibristels (SSSA, 2003) which correspond to Turbi-leptic, Turbi stagnic and Organo-turbic Cryosols (ornithogenic) (Tarnocai et al., 2004).

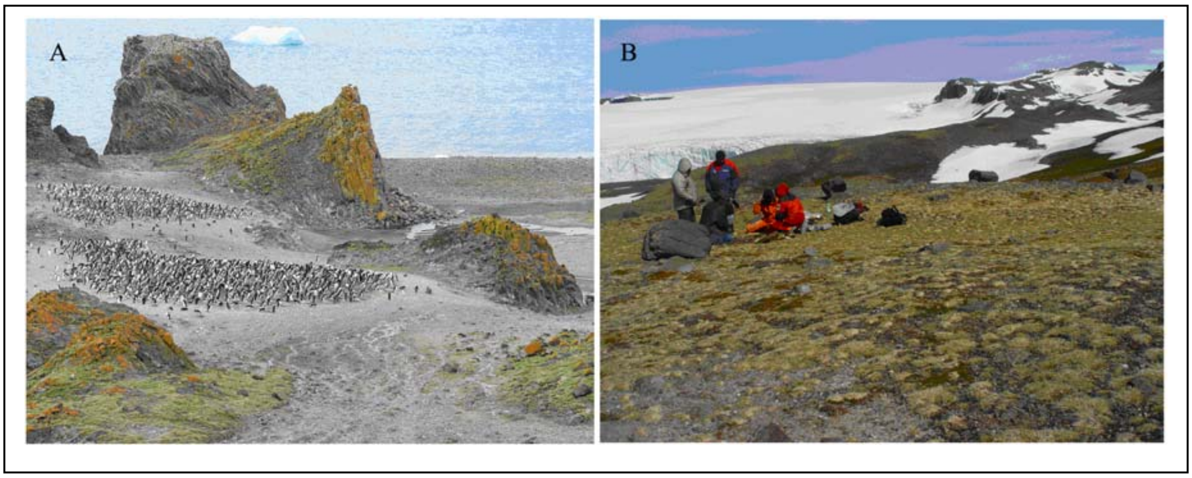

Figure 8 – Active penguin rookeries at Rakusa Point (left). Intense trampling and guano deposition by birds inhibit vegetation development. Orange ornithocoprophilous lichens are common on rock outcrops surrounding the rookery. Abandoned penguin rookeries are covered with well-developed vegetation (right).

4. Summary and conclusions

The data presented in this work suggest that physical weathering and cryoturbation are both major processes in ice-free areas of Admiralty Bay. In general, soils are poorly developed with physical, chemical and morphological characteristics strongly related to the parent material. In localized areas, the acidolysis promoted by sulphide oxidation enhances chemical weathering. Similarly, the decomposition of bird guano leads to soil acidification and enhance plant development at ornithogenic sites.

Although most soils were adequately classified, it was necessary to include the *ornithogenic* qualifier in both classification systems in order to classify soils affected by penguins. The *sulphuric* qualifier had to be included in the Haploturbel sub-order for a more adequate classification of acid sulphate soils.

Greyish colored, eutric Lithic and Typic Haploturbels (Thurbi-leptic Cryosols) with neutral to alkaline reaction nature are the most common soils in Admiralty Bay. Sulphuric Haploturbels (Turbi-thionic Cryosols) are restricted to areas affected by veins of pyritized andesite found in Keller Peninsula and Crépin Point. Umbriturbels (Turbi-umbric Cryosols) only occur at sites under bird influence. Ornithogenic Gelisols and Cryosols are the most developed soils in Admiralty Bay with pronounced alteration of parent materials and formation of phosphatic B horizons. Ornithogenic Fibristels (Organo-turbic Cryosol (ornithogenic)) are restricted to poorly drained areas in the vicinities of penguin rookeries.

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CAPÍTULO 2

Ornithogenic Cryosols from Maritime Antarctica: phosphatization as a soil forming process

Abstract

Birds nesting activity during the short antarctic summer promotes intense localized sea-land transference of nutrients and organic matter, originating ornithogenic soils. This study presents chemical, physical and mineralogical data as well as some micropedological and submicroscopical characteristics of ornithogenic and non-ornithogemic soils from the western coast of the Admiralty Bay, King George Island. Chemical analysis of selected soil attributes show P and N enrichment in ornithogenic soils. Vegetation growth is enhanced resulting in high soil organic C contents. A granular, sub-rounded structure composed by silt particles surrounded by illuvial phosphates is typical at ornithogenic horizons. These illuviation features characterize a distinct process of phosphatization, with P mobility and neoformation of secondary phosphates, such as Taranakite, Minyulite and Leucophosphite. Ornithogenic sites are extremely important and constitute the most important locci of C sequestration in antarctic terrestrial ecosystems. A classification scheme for ornithogenic soils is proposed within the Soil Taxonomy and WRB classification systems.

Keywords: Cryosols, Antarctica, Phosphatization, Soils, Classification

1. Introduction

Intense penguin activity on ice-free areas along the Antarctic coast leads to the formation of the so-called *ornithogenic* soils (Ugolini, 1970; Ugolini, 1972; Campbell and Claridge, 1987; Tatur, 1989). According to Ugolini (1972), guano accumulation in penguin rookeries represents the most abundant source of organic matter in the Antarctic terrestrial ecosystem. At dryer and colder continental parts of Antarctica, ornithogenic soils are characterized by a sharp boundary between the guano layer and the underlying mineral horizon (Ugolini, 1972; Campbell and Claridge, 1987). In these extremely cold, arid environments, guano deposition apparently has little influence on mineral alteration (Ugolini, 1972).

On the other hand, in Maritime Antarctica, warmer temperatures and higher water availability result in intense cryoturbation with deep mixing of bird detritus within the soil. P-rich percolates react with the mineral substrate in a particular and complex process of soil “phosphatization”, described in detail by Tatur and Barczuk (1985). Chemical weathering is enhanced at these sites, with formation of crystalline and amorphous secondary P minerals (Myrcha et al., 1985; Tatur and Barczuk, 1985; Tatur, 1989; Tatur and Myrcha, 1993; Tatur et al., 1997; Schaefer et al., 2004). At sites adjacent to penguin rookeries, high amounts of amorphous, P-rich minerals are formed which control soil chemical characteristics (Chapter 3). Skuas (*Catharacta sp.*) and other flying birds which nest around the penguin rookeries also expand the ornithogenic influence further away (Ugolini, 1972).

Despite their recognized scientific and ecological importance, ornithogenic soils are not keyed in the current Soil Taxonomy (SSSA, 2003) and *World Reference Base for Soil Resources (WRB)* (ISSS Working Group RB, 1998) classification systems. Thus, the inclusion of the *ornithogenic* character seems appropriate for a more adequate classification of these unique, endemic soils (Bockheim, 2005).

The aim of this work is to assess the impact of penguin activity on terrestrial ecosystems of Maritime Antarctica. Several sites with different degrees of ornithogenic influence were studied at Admiralty Bay, King George Island. Chemical, physical, mineralogical and micromorphological properties are discussed, and a new classification scheme for ornithogenic soils is proposed.

2. Material and Methods

2.1 Study area

Admiralty Bay (62^{o}03’40”- 62^{o}05’40” S and 58^{o}23’30” - 58^{o}24’30” W) is located in King George Island, South Shetlands Archipelago, Maritime Antarctica (Figure 1). Data sets from 1982-2002, acquired at the Brazilian Comandante Ferraz Station, report mean air temperatures varying from -6.4 ^{o}C in July to +2.3 ^{o}C in February. Mean annual precipitation is 366.7 mm. Positive air temperatures are observed from November to March when effective precipitation as liquid water is increased due to melting of accumulated winter snow.

Soils were collected in the vicinity of the Polish Henry Arctowski Station at the western coast of the Admiralty Bay (Figure 1). They are formed predominantly from Tertiary tholeite basalts and related moraine, solifluction and fluvioglacial deposits. Several data indicate that deglaciation at King George Island occurred ~ 6000 years ago and a climatic optimum occurred between ca. 4000 and 3000 years ago (Bjorck et al., 1991; Yoon et al., 2000). Occasional deposition of volcanic ash has also been reported (Blume et al., 2004; Jeong and Yoon, 2001).

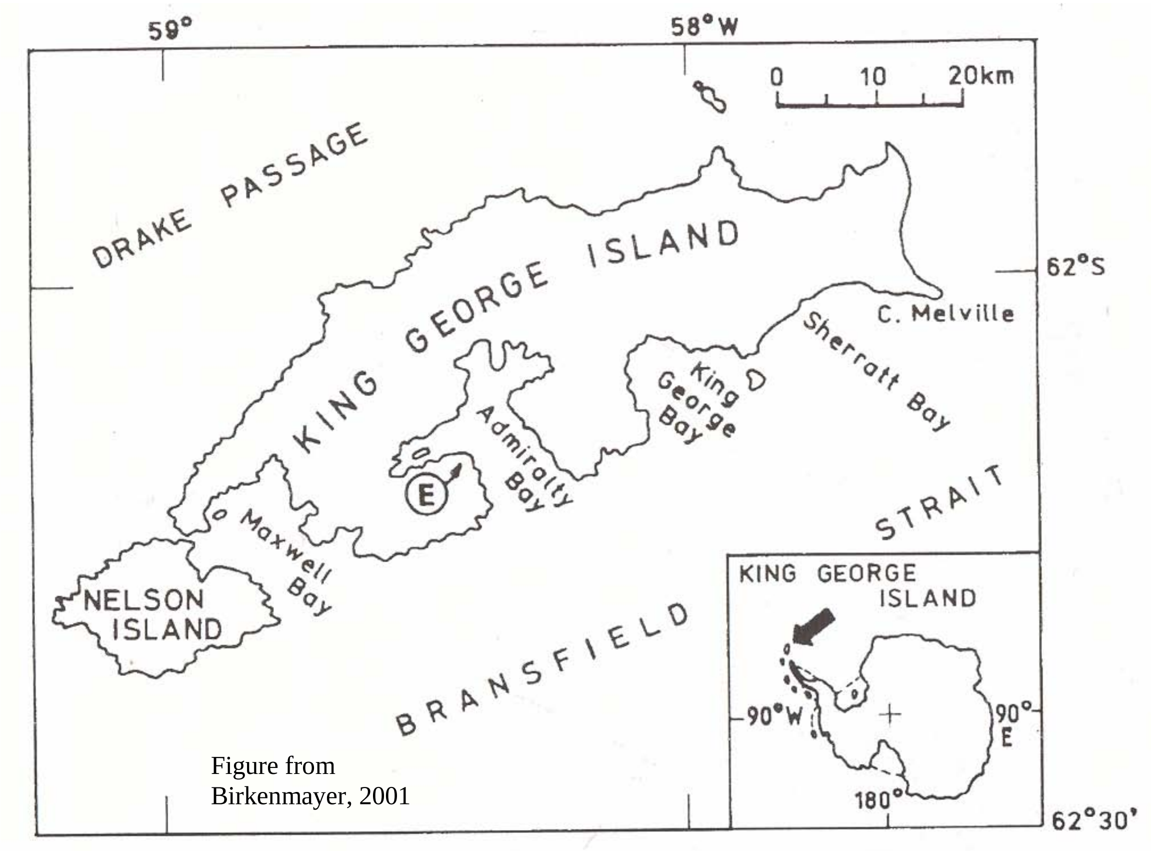

Figure from
Birkenmayer, 2001

Figure 1 – The Admiralty Bay, King George Island. The letter E indicates the approximate location of the investigated sites.

2.2 Soil sampling

In order to investigate the impact of penguin activity on soil characteristics and vegetation establishment, an altitudinal sequence of ten sites with different degrees of ornithogenic influence was studied. General characteristics and the geographic position of the studied sites are given in Table 1. Soil classification followed the Soil Taxonomy (*ST*) (SSSA, 2003) and *World Reference Base for Soil Resources (WRB)* (ISSS Working Group RB, 1998) classification systems. Suggestions of new soil classes are discussed later in this publication.

Table 1 –General characteristics of the different sites.

Site	**Pedon**	**Alt. (m.s.l.)**[1]	**Vegetation**[2]	**Soil Classification**[3]	**Description**	**Geographic position** [4]
1	A10	147	Absent	Typic Haploturbel * Turbic Cryosol **	Subpolar desert without any ornithogenic influence. Desert pavement overlying oxidized basaltic till. Virtually no horizonation. Single grain and medium granular structure.	422642 West 3107137 South
2	A9	87	D > C	Lithic Haplorturbel* Turbi-Leptic Cryosol**	Skua nest in subpolar desert with weak ornithogenic influence. Discontinuous vegetation with occurrence of higher plants (*Deschampsia antarctica* and *Prasiola* crispa). Formation of a shallow, incipient A horizon. Single grain and medium granular structure.	422918 W 3106982 S
3	A4	72	D > C	Typic Psammoturbel* Hapli-Turbic Cryosol**	Abandoned rookery on the highest level of ornithogenic influence, probably the most ancient level of ornithogenic soil. Continuous vegetation cover. Well defined A ,B and C horizons. Crumbs in A and medium granular structure in B. Ice-cemented permafrost starting at 45 cm.	423593 W 3106696 S
4	A3	69	D > M > C	Typic Psammoturbel* Skeleti-Turbic Cryosol**	Abandoned, well-drained penguin. Well defined A horizon below a continuous vegetation cover. Phosphatization evidenced by whitish discontinuous B horizon starting at 20 cm. Crumbs in A. Single grains and medium granular structure in B. Ice–cemented permafrost at 50 cm.	423514 W 3106710 S
5	A6	50	D > M> C> L	Andic Umbriturbel* Umbri-Turbic Cryosol**	Close to site 7 but with a longer time of abandonment as evidenced by the well developed vegetation cover and presence of A horizon. Ice-cemented permafrost at 60 cm.	423741 W 3106706 S
6	A1	45	D > L	Andic Umbriturbel* Umbri-Turbic Cryosol**	Well drained uplifted terrace, at the lower part of a slope. Continuous vegetation cover and well defined A horizon. Indirect penguin influence through lateral percolates from former rookeries.	423344 W 3106855 S
7	A5	45	P	Typic Haploturbel* Andi-Turbic Cryosol**	Represents the most recently abandoned rookery, adjacent to the current penguin nesting area. Incipient A horizon, below a well-developed *Prasiola crispa* cover. Ice-cemented permafrost at 65 cm.	423736 W 3106702 S
8	A2	32	M > D	Psammentic Aquiturbel* Oxyaqui-Turbic Cryosol**	Similar to site 6 but poorly drained, with predominance of mosses. This site receives a high amount of leacheates from upslope rookeries.	423415 W 3106099 S
9	A7	23	M > D	Terric Fibristel* Turbi-Histic Cryosol**	Moss peat on uplifted marine terrace. Fibric, 50 cm deep, O horizon overlying a mineral horizon. Ice-cemented permafrost at 70 cm from the soil surface.	423687 W 3106809 S
10	A8	5	D >M > C	Andic Cryofluvent Gelic Fluvisols	Marine terrace under strong influence of nutrient-rich leacheates from upslope penguin rookeries. Frequent occurrence of phosphatic, white precipitates on rock surfaces. Single grain structure.	423918 W 3106799 S

[1]meters above sea level;[2] M – mosses; L – lichens; D – *Deschampsia antarctica* ; C – *Colobanthus quietensis*; [3] * Soil taxonomy, ** WRB; [4] UTM coordinates, zone 21S datum WGS 84.

2.3 Chemical, physical and mineralogical analyses

Routine chemical and physical analyses were carried out in air-dried < 2mm samples, according to the methods described in Chapter 1. Hedley's sequential extraction (Hedley et al., 1982), modified by Araújo et al. (2004), was used to fractionate soil P into the following inorganic (Pi) and organic (Po) pools, of decreasing availability to plants: a) anionic resin-Pi; $NaHCO_3$ Pi and Po; b) NaOH Pi and Po (includes P associated to Al and Fe oxides); c) H_2SO_4-Pi (apatite and other recalcitrant Ca phosphates) and; d) residual P (most resistant P forms). The extraction procedure is described below:

Samples (0.5 g) were extracted in the following order, using 30 ml of extractant and 16 h shaking time: (1) resin-Pi - deionised water and one 1x7 cm resin strip (ANION 204UZRA); (2, 3) $NaHCO_3$ Pi and Po - 0.5 mol/L $NaHCO_3$; (4,5) NaOH Pi and Po - 0.1 mol/L NaOH; (6) H_2SO_4 Pi – extracted with 1 mol/L H_2SO_4; (7) residual P – H_2SO_4/H_2O_2 digestion at 360 ^oC. $NaHCO_3$ and NaOH extracts were divided into two aliquots and the total P (Pt) in each extract ($NaHCO_3$ and NaOH) was determined after addition of 1 ml of 24 mol/L H_2SO_4, 0.2 g of $K_2S_2O_8$ and digestion at 127^{o}C for 1 hour. Pi was determined for aliquots without previous digestion and the organic P (Po) was determined by difference (ex. Po $NaHCO_3$ = Pt $NaHCO_3$ – Pi $NaHCO_3$). The total P represents the sum of all extracted fractions. All P measurements were made by photocolorimetry according to Murphy and Riley (1962).

Clay fraction mineralogy was studied by chemical dissolution and X-ray diffraction (XRD). The < 2mm soil samples were submitted to the following extractions:

(i) pH 10.0 Na-pyrophosphate (pyr) - extraction of organic matter bound Al and Fe (Dahlgren, 1994);

(ii) pH 3.0 0.2 mol/L ammonium oxalate in the dark (ox) - extraction of poorly ordered Fe oxides (Schwertmann, 1973) and amorphous allophane-like Al and Si minerals (Campbell and Schwertmann, 1985);

(iii) Ditionite-citrate - extraction of pedogenic Al and Fe oxides (McKeague and Day, 1966).

Aproximately 0.5 g of finely ground, untreated, dry clay samples were mounted on aluminium holders and submitted to XRD analysis. The XRD patterns were obtained using monochromated CuKα radiation and were interpreted according to Brindley and Brown (1980) and Nriagu and Moore (1984).

2.4 Optical transmission (OTM) and scanning electron microscopy (SEM)

Undisturbed soil blocks (5x10 cm) from sites 3 and 4 were impregnated with a 1:1 crystic resin:stiren mix poured onto samples at atmospheric pressure. Impregnated samples were cut into slabs of 0.5 cm thickness using a diamond saw, and polished with corundum 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 30nm thick sections. No cover slips were used. Thin sections were examined under a Zeiss polarizing microscope (OM level) using an attached Pentax camera fitted with a Zeiss exposure-meter.

Pedological features of the pedogenic horizons at OM level, such as structural units, porosity, presence of pedofeatures (nodules, concrections) were analysed using standard micromorphological techniques (Bullock et al., 1985). The microstructure and submicrostructure were investigated using a JEOL 6400 scanning electron microscope coupled with an Oxford Instruments energy dispersive X-ray detector (SEM/EDS). Flat ultrapolished, uncovered thin sections of approximately 18 cm^2 were analysed for the elemental distribution of Si, Al, Fe, Mn, Ti, Mg and trace-elements across individual peds and phosphate infillings and cutans, using EDS and wavelength dispersive spectrometry (WDS). In this paper, only major element data are reported.

3. Results and discussion

3.1 Soils morphological and physico-chemical characteristics

Site 1 - non-ornithogenic soil

The soil from site 1 is eutric and has a medium-sized, granular structure, below a stony pavement. Na levels are extremely high (Table 2) due to sea spray deposition and reduced leaching suggesting accumulation of water-soluble salts, although macroscopic salt efflorescence is not observed. The high soil pH and exchangeable Ca^{2+} and Mg^{2+} for this site (Table 2) are consistent with the geochemistry of the basaltic parent rock. The level of P extractable with Mehlich-1 is the lowest of all studied sites (Table 2). Due to the complete absence of vegetation, TOC is extremely low and total nitrogen is negligible (Table 2).

The morphology of this pedon resembles that described for soils from continental Antarctica, being rather featureless and with virtually no horizonation (Ugolini, 1972; Campbell and Claridge, 1987, 2004a and 2004b). Brownish colours (10 YR 5/2 and 5/3) dominate throughout the profiles (Table 3) and are related to the oxidation of primary mafic minerals in the basaltic parent rock. The content of silt + clay particles increases with depth indicating cryoturbation (Table 3). Strong translocation of fine particles can occur on tills under high precipitation and frequent frost action leading to the development of B silt layers (Frenot et al., 1995), which seems to be occurring in this soil.

Site 2 – soil with weak ornithogenic influence

Site 2 is located in the same landscape, only a few hundred meters from site 1 (Table 1). It is a shallow soil, with a lithic contact within 50 cm depth and is classified as a Lithic Haploturbel (*ST)* or Turbi-Leptic Cryosol (*WRB).* Scattered bone and egg shell fragments, nest remains and bird droppings evidence current nesting activity by skuas at this site and indicate an initial stage of ornithogenic influence. These flying birds feed on penguin rookeries and nest on higher areas expanding the ornithogenic influence.

A discontinuous vegetation community composed of lichens (*Usnea sp.*) and higher plants (*Colobanthus quietensis* and *Deschampsia antarctica*) is present. The soil has a lower pH and lower levels of exchangeable Ca, Mg and K in relation to site 1, while exchangeable Al, TOC, N and P are higher (Table 2). These data indicate that the guano deposition by skuas has promoted soil acidification, leaching of bases and formation of exchangeable Al^{3+}. Soil P and N enrichment favours vegetation establishment with the occurrence of higher plants, which results in much higher TOC values than at site 1 (Table 3). Similarly to site 1, Na levels are high suggesting accumulation of soluble salts at this uppermost, drier pedoenvironments.

The similar values for effective and potential CEC (CEC_{eff} and CEC_{pot}) for both sites 1 and 2 are due to the predominance of permanently charged 2:1 clay minerals as discussed later in this paper (section 3.4). When the CEC_{eff} for the clay fraction is calculated (data not show), values as high as 400 $cmol_c$/kg of clay are obtained. These are much higher than that commonly reported for smectites (150 $cmol_c$ /kg), suggesting that water soluble salts were dissolved by the extractions.

Sites 3 to 10 - ornithogenic soils

Soils morphological characteristics, with clear horizon differentiation, indicate a higher degree of pedogenesis at ornithogenic sites when compared to sites 1 and 2. Cryoturbation is evidenced by the frequently discontinuous soil horizons with undulating boundaries. A stony/pebbly pavement is present at all sites but is often hidden by the well-developed, continuous vegetation. Dark brown and yellowish brown colours are observed at surface horizons as a result of continuous organic C incorporation (Table 3). Light brown and greyish colours for soils formed at former penguin rookeries (Table 3 - sites 3, 4, 5 and 7) evidence accumulation of secondary phosphates (Tatur and Barczuk, 1985; Myrcha et al., 1985), especially below 20 cm.

The ornithogenic soils are readily distinguished from the non-ornithogenic soil at site 1 by several features such as the presence of continuous vegetation cover with *Deschampsia antarctica*, *Colobanthus quitensis* and/or *Prasiola crispa*; lower pH and bases saturation (PBS); very high P, Al^{3+}, TOC and total N (Table 2). Higher extractable K and Na at site 7 are related to recent penguin activity, with deposition of K and Na-bearing urates (Tatur and Myrcha, 1993).

Deposition of P and N-rich guano favours vegetation establishment. The type of vegetation is strongly influenced by the duration of site occupation by penguins and soil drainage characteristics. Similarly to data reported for other ornithogenic sites of Antarctica, no vegetation is present at active rookeries due to the intense trampling by penguins and to the extremely aggressive composition of fresh guano (Ugolini, 1970; Ugolini, 1972; Tatur, 1989; Michel et al., 2006). At sites recently abandoned by penguins, the vegetation succession is initiated by the rapid establishment of continuous nitrophilic green algae (*Prasiola crispa*) mats. At poorly drained areas, exuberant moss carpets are formed, while at well-drained sites the higher plants *Deschampsia antarctica* and *Colobanthus quitensis* are frequent.

Table 2 – Some chemical attributes of the studied soils.

Hor.	**Depth**	**pH**	**P[1]**	**K[1]**	**Na[1]**	**Ca[2]**	**Mg[2]**	**Al[2]**	**H+Al[3]**	**BS[4]**	**CEC$_{eff}$[5]**	**CEC$_{pot}$[6]**	**PBS[7]**	**TOC[8]**	**N[9]**	**C/N**
	cm		**mg/dm^3**			**cmolc/dm^3**							**%**	**g/kg**		
Site 1 - pedon A10 - Typic Haploturbel /Turbic Cryosol																
C$_1$	0-10	6.6	65.0	115.0	1360.0	22.5	15.3	0.0	3.6	44.0	44.4	47.6	92.4	1.0	-	-
C$_2$	10-20	7.0	48.2	148.0	1440.0	29.8	21.4	0.0	2.3	57.8	57.9	60.1	96.2	1.0	-	-
Site 2 -pedon A9 - Lithic Haplorturbel/Turbi-Leptic Cryosol																
A	0-10	5.8	107.6	55.0	1260.0	12.9	6.9	1.4	9.9	25.4	26.8	35.3	71.9	17.0	2.1	8.1
Site 3 – pedon A4 - Typic Psammoturbel/Hapli-Turbic Cryosol																
O	10-0	-	-	-	-	-	-	-	-	-	-	-	-	22.0	3.5	6.2
A	0-15	4.2	1325.2	680.0	332.0	2.0	0.3	7.5	34.7	5.5	13.0	40.2	13.6	10.0	2.3	4.3
Bi$_1$	15-30	4.1	1143.9	660.0	286.0	3.1	0.7	9.8	38.3	6.8	16.6	45.1	15.1	5.0	-	-
BC	30-40	4.1	849.0	680.0	274.0	4.9	1.5	11.3	40.3	9.4	20.7	49.7	18.8	5.0	-	-
C	40-50	4.2	742.9	660.0	248.0	5.8	2.5	13.5	36.3	11.1	24.6	47.4	23.4	4.0	0.8	5.0
Site 4 – pedon A3 - Typic Psammoturbel/Skeleti-Turbic Cryosol																
A$_1$	0-10	4.6	828.4	179.0	180.0	4.3	2.6	3.3	17.3	8.2	11.5	25.5	32.1	15.0	1.8	8.4
A$_2$	10-20	4.3	1538.8	182.0	191.0	2.8	1.0	5.4	19.0	5.1	10.5	24.1	21.2	8.0	6.4	1.3
Bi$_1$	20-30	3.9	1454.3	214.0	173.0	2.3	0.5	7.1	29.7	4.2	11.3	33.9	12.3	14.0	2.4	5.9
Bi$_2$	30-40	3.9	1401.0	144.0	98.0	1.7	0.3	6.9	3.4	2.8	9.7	13.1	2.1	14.0	3.3	4.2
BC$_1$	40-50	3.9	1793.4	180.0	132.0	1.8	0.2	6.9	26.6	3.1	10.0	29.7	10.4	13.0	-	-
BC$_2$	50-60	4.0	1652.6	176.0	131.0	0.4	0.9	7.7	29.2	2.4	10.1	31.6	7.5	14.0	-	-
C	60-70	3.9	1283.8	129.0	90.0	2.2	0.4	6.3	24.6	3.4	9.7	28.0	12.0	13.0	9.6	1.4
Site 5 – pedon A6 - Andic Umbriturbel/Umbri-Turbic Cryosol																
A$_1$	0-10	4.6	2466.2	132.0	290.0	8.5	5.6	2.7	17.2	15.7	18.4	32.9	47.8	24.0	4.0	6.0
A$_2$	10-20	4.6	3910.9	184.0	306.0	4.7	2.0	2.6	16.7	8.6	11.2	25.3	33.9	20.0	4.2	4.7
Bi	20-30	4.5	4156.5	380.0	320.0	7.7	1.8	3.1	28.2	11.8	14.9	40.0	29.5	13.0	3.5	3.7
BC	30-40	4.4	3242.0	410.0	310.0	8.9	1.3	4.5	26.9	12.6	17.1	39.5	31.9	13.0	4.4	2.9
C	40-60	4.1	1932.8	300.0	280.0	9.6	1.2	8.4	28.5	12.8	21.2	41.3	31.1	12.0	-	-

[1] Melich-1 extractable P, K and Na; [2]exchangeable Ca^{+2}, Mg^{+2} and Al^{+3}; [3]extracted with 0.5 mol/L calcium acetate at pH 7.0; [4]bases sum; [5]effective cation exchange capacity; [6]CEC at pH 7.0; [7]percentage of bases; [8]Total organic carbon; [9]Total nitrogen; D – desert pavement; - below the detection limit.

Table 2 – Cont….

Hor	**Depth**	**pH**	**P^1**	**K^1**	**Na^1**	**Ca^2**	**Mg^2**	**Al^2**	**H+Al^3**	**BS^4**	**CEC$_{eff}$^{5}**	**CEC$_{pot}$^{6}**	**PBS^7**	**TOC^8**	**N^9**	**C/N**
	Cm		**mg/dm^3**			**cmolc/dm^3**							**%**	**g/kg**		
Site 6 – pedon A1 - Andic Umbriturbel/Umbri-Turbic Cryosol																
1A$_1$	0-10	5.7	60.8	77.0	420.0	7.9	1.5	0.4	6.4	11.4	11.8	17.8	64.1	29.0	15.2	1.9
1A$_2$	10-20	5.5	70.1	71.0	740.0	12.1	8.8	1.1	7.4	24.3	25.4	31.7	76.6	24.0	13.7	1.8
2Bi$_1$	20-30	5.7	218.9	87.0	380.0	16.0	11.4	0.7	9.1	29.3	30.0	38.4	76.3	9.0	5.1	1.8
2BC$_1$	30-40	5.5	282.1	102.0	300.0	14.5	9.5	8.4	17.0	25.6	34.0	42.6	60.1	5.0	3.3	1.5
2BC$_2$	40-50	5.2	384.8	105.0	328.0	11.0	7.6	12.4	25.1	20.3	32.7	45.4	44.7	6.0	-	-
2C$_1$	50-60	5.2	412.0	111.0	324.0	8.4	6.2	12.9	27.7	16.3	29.2	44.0	37.1	-	-	-
2C$_2$	60-70	5.2	418.8	118.0	346.0	8.9	4.9	19.1	27.9	15.6	34.7	43.5	35.8	-	-	-
Site 7 – pedon A5 - Typic Haploturbel/Andi-Turbic Cryosol																
A	10-20	4.5	4271.3	520.0	660.0	13.1	2.4	5.1	38.9	19.7	24.8	58.6	33.6	26.0	5.1	5.1
BC	20-30	3.8	1734.0	1060.0	280.0	7.4	1.4	13.0	34.8	12.8	25.8	47.6	26.9	7.0	4.8	1.5
C	30-40	3.8	1544.4	990.0	176.0	9.7	3.7	10.4	43.4	16.6	27.0	60.0	27.7	7.0	3.1	2.2
Site 8 –pedon A2 - Psammentic Aquiturbel/Oxyaqui-Turbic Cryosol																
A	0-10	5.9	251.8	84.0	366.0	9.4	0.9	2.4	14.2	12.1	14.5	26.3	46.1	48.0	20.0	2.4
Bi$_1$	10-20	4.8	436.3	77.0	248.0	8.3	4.3	5.4	17.8	13.9	19.3	31.7	43.8	15.0	1.6	9.3
Bi$_2$	20-30	4.9	385.9	98.0	208.0	7.4	4.1	6.5	20.5	12.6	19.1	33.1	38.0	12.0	1.3	9.5
BC$_1$	30-40	4.9	490.0	122.0	248.0	6.0	3.3	10.4	24.1	10.8	21.2	34.9	30.9	7.0	1.1	6.5
C	40-50	4.9	826.2	129.0	252.0	10.0	5.4	3.3	23.4	16.9	20.2	40.3	41.9	8.0	1.0	7.9
Site 9 – pedon A7 Terric Fibristel/Turbi-Histic Cryosol																
O$_1$	50-40	4.3	658.4	80.0	150.0	2.8	0.8	7.2	22.4	4.5	11.7	26.9	16.7	44.0	6.4	6.9
O$_2$	40-30	4.2	667.6	72.0	151.0	1.8	0.4	7.6	26.7	3.0	10.6	29.7	10.1	35.0	4.9	7.1
O$_3$	30-20	4.2	904.3	101.0	170.0	2.2	0.5	12.6	32.7	3.7	16.3	36.4	10.2	22.0	3.2	7.0
O$_4$	20-10	4.3	1117.3	81.0	155.0	2.5	0.6	12.1	36.3	4.0	16.1	40.3	9.9	29.0	2.2	13.4
O$_5$	10-0	4.3	1030.9	81.0	172.0	2.6	0.6	11.7	31.4	4.2	15.9	35.6	11.7	33.0	3.0	10.8
B$_1$	0-20	4.3	999.4	74.0	133.0	2.4	0.5	12.3	41.9	3.7	16.0	45.6	8.2	32.0	-	-
B$_2$	20-30	4.2	891.9	84.0	156.0	2.4	0.6	10.9	28.4	3.9	14.8	32.3	12.0	21.0	2.2	9.5
Site 10 –pedon A8 - Andic Cryofluvent/Gelic Fluvisols																
A	0-10	-	-	-	-	-	-	-	-	-	-	-	-	28.0	7.9	3.6
C$_1$	10-20	4.4	626.1	780.0	125.0	2.2	1.0	2.7	18.3	5.7	8.4	24.0	23.7	20.0	9.2	2.2
C$_2$	20-30	4.3	302.8	510.0	132.0	2.0	0.8	3.0	14.4	4.7	7.7	19.1	24.4	16.0	12.3	1.3

[1] Melich-1 extractable P, K and Na; [2]exchangeable Ca^{+2}, Mg^{+2} and Al^{+3}; [3]extracted with 0.5 mol/L calcium acetate at pH 7.0; [4]bases sum; [5]effective cation exchange capacity; [6]CEC at pH 7.0; [7]percentage of bases; [8]Total organic carbon; [9]Total nitrogen; D – desert pavement; - below the detection limit.

Table 3 – Soil colour and texture for the different sites.

Hor	Depth	Munsell Colour		Skel[1]	sand		silt	clay
	cm	dry soil		(%)	c.[2]	f.[3]	(%)	
Site 1 – pedon A10 - Typic Haploturbel/Turbic Cryosol								
C_1	0-10	10YR 5/2	greyish brown	36	62	7	17	14
C_2	10-20	10YR 5/3	brown	-	37	14	33	16
Site 2 – pedon A9 - Lithic Haploturbel/Turbi-Leptic Cryosol								
A	0-10	10YR 4/3	brown	58	64	11	14	11
Site 3 – pedon A4 - Typic psammoturbel/Hapli-Turbic Cryosol								
O	0-10	-	-	66	63	9	17	11
A	10-20	7,5 YR 6/1	grey	-	55	13	20	12
Bi_1	20-30	10 YR 4/3	brown	-	53	17	22	8
BC	30-40	10 YR 4/3	brown	36	59	14	18	9
C	40-50	10 YR 4/3	brown	-	61	14	18	7
Site 4 – pedon A3 - Typic psammoturbel/Skeleti-Turbic Cryosol								
A_1	0-10	10YR 5/3	brown	49	87	4	3	6
A_2	10-20	10YR 5/3	brown	-	88	4	3	5
Bi_1	20-30	10YR 6/4	light yellowish brown	-	81	4	8	7
Bi_2	30-40	10YR 7/3	very pale brown	51	71	6	12	11
BC_1	40-50	10YR 6/4	light yellowish brown	-	83	5	6	6
BC_2	50-60	10YR 6/3	pale brown	-	73	7	13	7
Site 5 – pedon A6 - Andic Umbriturbel/Umbri-Turbic Cryosol								
A_1	0-10	7,5 YR 5/3	brown	95	63	11	14	12
A_2	10-20	10YR 7/3	very pale brown	-	63	10	15	12
Bi	20-30	2,5Y 6/2	light brownish grey	-	65	10	13	12
BC	30-40	2,5Y 7/2	light grey	69	62	10	16	12
C	40-60	2,5Y 7/2	light grey	-	60	8	16	16
Site 6 – pedon A1 - Andic Umbriturbel/Umbri-Turbic Cryosol								
1^a_1	0-10	7,5YR 3/4	dark brown	31	57	9	17	17
$1A_2$	10-30	7,5YR 4/3	brown	-	59	12	14	15
$2Bi_1$	30-40	7,5YR 4/3	brown	58	63	11	14	12
$2BC_1$	40-50	10 YR 5/3	brown	-	69	14	8	9
$2BC_2$	50-60	10YR 5/4	yellowish brown	-	61	15	13	11
$2C_1$	60-70	10YR 5/4	yellowish brown	-	56	15	18	11
$2C_2$	70-80	10YR 5/4	yellowish brown	-	57	9	17	17

[1] % of particles > 2 mm; [2] coarse sand; [3] fine sand; - not determined.

Table 3 – Cont.

Hor	**Depth**	**Munsell Colour**		**Skel**[1]	**sand**		**silt**	**clay**
	cm	**dry soil**		**(%)**	**c.**[2]	**f.**[3]	**(%)**	
Site 7 – pedon A5 - Andic Umbriturbel/Andi-Turbic Cryosol								
A_1	0-10	2,5Y 7/2	light grey	69				
A_2	10-20	10YR 6/3	pale brown	-	53	9	22	16
BC	20-30	10YR 7/2	light grey	-	33	12	35	20
C	30-40	7,5YR 4/1	dark grey	82	42	14	28	16
Site 8 – pedon A2 - Psammentic Aquiturbel/Oxyaqui-Turbic Cryosol								
A	0-10	10YR 4/4	dark yellowish brown	47	69	6	14	11
Bi_1	10-20	10YR 4/3	brown	-	80	3	7	10
Bi_2	20-30	10YR 5/2	grayish brown	-	74	9	9	8
BC	30-40	10YR 6/2	light brownish grey	57	71	9	10	10
C	40-50	10YR 6/2	light brownish grey	-	74	5	9	12
Site 9 – pedon A7 - Terric Fibristel/Turbi-Histic Cryosol								
O_1	50-40	7,5YR 4/4	brown	31	59	7	20	14
O_2	40-30	7,5YR 4/4	brown	-	47	12	27	14
O_3	30-20	7,5YR 4/3	brown	-	59	13	16	12
O_4	20-10	7,5YR 4/4	brown	18	72	8	11	9
O_5	10-0	7,5YR 4/4	brown	-	69	7	13	11
B_1	0-20	7,5YR 4/4	brown	-	70	8	15	7
B_2	20-30	7,5YR 4/4	brown	-	72	9	12	7
Site 10- pedon A8 - Lithic Umbriturbel/Gelic Fluvisols								
A	0-10	-	-	68	67	8	14	11
C_1	10-20	2,5Y 7/2	light grey	-	55	8	20	17
C_2	20-30	2,5Y 7/2	light grey	67	50	7	25	18

[1] % of particles > 2 mm; [2] coarse sand; [3] fine sand; - not determined; - not determined

All ornithogenic soils have much higher TOC values than the non-ornithogenic soil from site 1. Sites dominated by *Deschampsia antarctica* and *Colobanthus quitensis* (sites 3, 4, 5 and 6) have higher TOC levels with depth due to the presence of lignine-bearing tissues and proper root systems. On the other hand, soils covered with *Prasiola crispa* or mosses have an abrupt reduction of TOC with depth (sites 7 and 8 respectively). Although biomass production by the Antarctic vegetation is relatively low, it frequently exceeds the decomposition capacity of local microbiota (Ugolini, 1972). Therefore, organic matter accumulates at some sites and plays important pedological and ecological roles (Beyer et al., 1995; Beyer, 2000; Bölter and Kandeler, 2004).

Site 9 represents a relict moss peat protected from erosion by a basaltic dyke following a NE-SO orientation. A fibric organic horizon overlies a well-developed mineral layer characterizing a Terric Fibristel (*ST)* or Turbi-Histic Cryosol (*WRB*). In the past landscape, rich percolates from upland surrounding rookeries enhanced soil fertility and favoured the development of moss carpets in this relatively poorly drained area. The frequent waterlogging during the thawing period favoured the preservation of poorly-decomposed moss remains with formation of the present thick, fibric horizons.

At Site 10, located in the lowest position of the altitudinal sequence, the marine terrace receives percolates and run-off water from upslope penguin rookeries. Melich-1 extractable-P is considerably lower (300-600 mg/dm^3) when compared to the other ornithogenic sites (Table 2). Part of the P is leached back to the sea through ravines and melt-water channels, as indicated by the whitish precipitates on rock surfaces down to the sea level.

3.2 – P fractions

Extraction with Melich-1

The Melich-1 extraction is a simple, relatively cheap method which is routinely used to assess P availability to plants in weathered, tropical soils where most of the soil P is strongly adsorbed to the surface of Al and Fe oxi-hydroxides. Due to its extremely acid reaction (pH < 2.0), Ca-P forms of reduced availability are also partially extracted.

The levels of P extracted with Melich-1 were higher for acid soils *directly* influenced by penguin activity (soils from abandoned penguin rookeries such as sites 3, 4, 5 and 7). The highest value was obtained for the first layers of the most recently abandoned rookery (Table 3, Site 7). High P values with depth for sites 4 and 5 indicate P illuviation after site abandonment by penguins.

Soils which receive run-off and percolating waters from penguin rookeries are indirectly affected by penguin activity (sites 6, 8, 9 and 10). In these soils, the values of Melich-1 extractable-P are lower and tend to increase with depth, except for site 10 (Table 3). At site 6, the P levels for the first 20 cm are very low, being comparable to those obtained for site 1. This indicates that a basaltic colluvium was deposited over the ornithogenic material by solifluction from upslope non-ornithogenic areas.

The results of the Melich-1 extraction clearly evidence the impact of ornithogenic activity in soil chemistry. In this specific soil sequence, the basaltic substrate with little ornithogenic influence (site 1), in which rock apatite is the primary P source, had a maximum Melich-1 extractable-P of 65.0 mg/dm^3. Incipient ornithogenic influence (skuas nest) at site 2 increased this value to 107.6 mg/dm^3 as a result of ornithogenic P inputs. The lowest P value for the ornithogenic soils was 218.9 mg/dm^3 for the 30-40 cm layer of site 6. Ornithogenic soils formed under indirect penguin influence (sites 6, 8, 9 and 10) presented mean Melich-1 P value of 595.0 (± 289.2) mg/dm^3.

For those soils formed under direct penguin influence (sites 3, 4, 5 and 7) a mean value of 1961.7 (± 1117.7) mg/dm^3 was obtained. The extremely high Melich-1 extractable-P for the highest and most ancient ornithogenic soil (Table 3-Site 3) indicates that P minerals constitute stable P reserves at these sites. A detailed study of clay -sized minerals for Antarctic soils with different degrees of ornithogenic influence is presented in Chapter 3.

P sequential extraction

Although the Melich-1 extraction proved to be a good method for a preliminary comparative evaluation of the ornithogenic degree for different soils and soil horizons, it only extracts the acid-soluble part of the soil P pool. On the other hand, the sequential extraction fractionates the total soil P in phases of different lability and therefore allows a better understanding of the phosphatization process.

The total P value for the non-ornithogenic soil (site 1) was 369.1 mg/kg (Table 4). Rock apatite (Ca-P), which is estimated by the H_2SO_4-Pi pool, appears as the primary source of P in this soil, followed by the moderately labile, most labile and residual fractions. Due to the very low organic matter content, the organic P pool is negligible. These results indicate that as primary Ca-P is transformed, a great part of the P is incorporated in secondary pedogenic minerals. As presented in Chapter 3, appreciable amounts of allophane-like phases are present in the clay fraction of this soil. These minerals are likely to form stable complexes with the P released from primary minerals.

For soils under indirect penguin influence (sites 6 and 8), the total P increases with depth ranging from 640.7 to 2,140.3 mg/kg for site 6 and from 3,811.2 to 5,491.2 mg/kg for site 8. This evidences an impressive increase of the soil total P pool when compared to the non-ornithogenic sites and also indicate P illuviation and accumulation with depth (Table 4). Moderately labile Al and Fe-P phases (Table 4, NaOH-Pi) are the main P fractions for both sites. This is in agreement with the data presented in Chapter 3, which indicates that most of the clay fraction in some ornithogenic soils is composed by Al and Fe phosphates, with high participation of amorphous and organic phases which are known for their high surface area and P affinity (Parfitt, 1989).

Due to the dominance of secondary P forms in subsurface, the relative amount of recalcitrant fractions (H_2SO_4 + Residual P) decreases with depth (Table 4). Site 6 presented the lowest labile inorganic P pool (Resin-Pi + $NaHCO_3$-Pi) of all ornithogenic soils, increasing abruptly with depth from 67.7 to 299.9 mg/kg. These results corroborate the idea that a basaltic P-poor colluvium has been deposited over a phosphatized horizon at this site. For site 8, the labile inorganic pool ranged from 504.0 to 722.9 mg/kg. These values are almost 10 times higher than that obtained for site 1 and indicate that P availability for biological activity is much higher at sites under ornithogenic influence. Consequently, the total organic P is also higher (Table 4).

Total P values as high as 13,592 mg/kg were obtained for soils from abandoned penguin rookeries (Table 4 – site 4). For sites 4 and 5, NaOH-Pi ranged from 3,527.3 to 10,691.5 mg/kg. Labile P phases ranged from 659.6 to 1,537.0 mg/kg, while recalcitrant phases (Ca-P + residual-P) represent a much lower portion of soils total P (Table 4). The organic P pool contains 1.0 to 6.8 % of the total P.

The highest accumulation of ornithogenic P occurs at sites which were once colonized by penguins and therefore directly influenced by these animals. Part of the P percolates through the profile and reacts with rock minerals to form stable secondary phases. A great part, though, is transported in surface melting water, lateral percolates or even as solid particles through solifluction or wind ablation, affecting the adjacent soils. The general distribution of the P pools is similar at sites directly and indirectly influenced by penguins but the magnitude is much higher for the former.

For the non-ornithogenic soils, the dissolution of lithogenic apatite (Ca-P) with formation of more labile fractions controls P availability. Due to the low chemical weathering degree of these soils, most of the P is still present as apatite. At ornithogenic sites, the heavy P input from guano deposition results in higher P values for all fractions, reaching impressive magnitudes at sites once colonized by penguins. The relative participation of more recalcitrant fractions is reduced by the ornithogenic influence and soils P availability is controlled by moderately labile phases (P bound to Al and Fe) which maintain extremely high levels of P available for biochemical processes. Our data indicates an increasing ornithogenic degree for the studied sites in the following order site 6 < site 8 < site 5 < site 4.

Table 4 – Sequential P extraction data with mean values for soil P pools for one non-ornithogenic soil and four ornithogenic soils with increasing degrees of phosphatization.

		Most labile			**Moderately labile**		**Recalcitrant**		
Hor	**Depth**	**Resin-Pi**[1]	**$NaHCO_3$-Pi**	**$NaHCO_3$-Po**[1]	**NaOH-Pi**	**NaOH-Po**	**H_2SO_4-Pi**	**Residual P**	**Total P**
	cm	**mg/kg**							
Non-ornithogenic soil									
Site 1 – pedon A10 - Typic Haploturbel /Turbic Cryosol									
C_1	0-10	20.6	26.3	0.0	79.5	0.0	199.6	35.9	361.9
Soils with indirect penguin influence									
Site 6 – pedon A1 - Andic Umbriturbel/Umbri-Turbic Cryosol									
A_1	0-10	20.5	47.2	18.0	131.2	53.9	234.7	135.2	640.7
$2B_1$	20-30	78.0	152.1	37.3	1000.3	135.0	639.9	101.7	2144.1
$2C_2$	50-60	121.8	178.1	8.1	1200.2	197.9	330.6	133.7	2170.3
Site 8- pedon A2 - Psammentic Aquiturbel/Oxyaqui-Turbic Cryosol									
A	0-10	170.7	333.7	65.6	2442.7	257.2	380.4	160.8	3811.2
Bi_2	20-30	272.2	287.0	79.1	2620.7	815.3	528.0	92.8	4695.1
C	40-50	316.4	406.5	81.4	4088.3	48.6	476.8	73.8	5491.8
Soil with direct penguin influence									
Site 5 – pedon A6 - Typic psammoturbel/Skeleti-Turbic Cryosol									
A1	0-10	471.9	429.9	325.2	6289.4	0.0	2020.2	161.0	9697.6
Bi	20-30	707.8	829.2	0.0	8041.5	107.5	654.9	67.4	10408.3
C	40-50	404.2	442.5	115.7	3527.3	0.0	634.7	90.5	5214.8
Site 4 – pedon A3 - Andic Umbriturbel/Umbri-Turbic Cryosol									
A1	0-10	243.4	416.2	138.1	5625.4	407.4	1093.4	100.2	8024.3
Bi_1	20-30	529.8	827.0	227.5	10691.5	74.9	1165.8	75.3	13591.7
C_2	50-60	417.2	515.2	271.8	9365.0	0.0	663.0	87.1	11319.2

[1] Pi and Po stand for inorganic and organic P, respectively.

3.3 – Soil mineralogy

The data presented in Chapter 3 evidence a very low degree of chemical alteration for site 1, with presence of plagioclase and pyroxene in the clay fraction. The high Al_o

and Fe_o levels for the < 2mm fraction suggest andic properties for this soil (Table 5) and is consistent with the data obtained for the clay fraction (Chapter 3). Well-crystallized pedogenic iron oxides are present as indicated by the low Fe_o/Fe_d ratio (0.20) for the C horizon. The negligible Al_p and Fe_p for site 1 were expected due to the extremely low TOC for this soil.

This soil type constitutes the main substrate for terrestrial biological activity in Admiralty Bay. Therefore, the comparison of its chemical and mineralogical properties with ornithogenic soils allows a better understanding of the impacts of faunal activity on the formation of terrestrial ecosystems. Once guano deposition occurs, the ornithogenic P is expected to react first with amorphous aluminosilicates due to their large surface area and high P affinity.

At all other sites studied in this work, poorly crystalline Fe minerals predominate as indicated by the very high Fe_o/Fe_d ratios (0.8 – 1.0). Due to the higher TOC values, a considerable part of the Al and Fe is present as organometallic complexes (Table 5). The comparison of sites 1 and 2 reveals that even a relatively low guano deposition (due to skuas activity) results in the chemical transformation of primary minerals. Soil acidification favour the transformation of weatherable mafic minerals and releases appreciable amounts of highly reactive, amorphous Fe minerals which react with ornithogenic P to form amorphous and crystalline Fe-P minerals.

The XRD patterns for the clay fraction of ornithogenic soils from former rookery sites show that phosphate minerals are the main crystalline phases (Chapter 3). No crystalline phosphates are present in the first 10 cm as evidenced by the lack of characteristic peaks. Below 20 cm, well defined leucophosphite peaks (0.762 nm, 0.679

nm, 0.599 nm and 0.306 nm) are typical for highly phosphatized horizons. Minyulite (0.560 nm) and metavariscite (0.433 nm, 0.277 nm) are also present.

There is a large difference between CEC_{eff} and CEC_{pot} for all ornithogenic soils, indicating the presence of pH-dependent charges (Table 2). Since neither kaolinite nor crystalline oxides are present, both organic compounds (high TOC) and poorly crystalline Al-Si and Fe minerals are the most likely sources of pH-dependent charges in these soils. Consistently, high Al_{ox} + 0.5 Fe_{ox} ratios indicate andic properties for all ornithogenic soils. $(Al_o\text{-}Al_p)/Si_o$ ratios ranged from 0.7 to 5.2 with predominance of 2.0-3.0 ratios (Table 5), suggesting the presence of Al-rich amorphous phases (Dahlgren, 1994). High Al_p and Fe_p levels suggest that organo-metallic compounds are major components of the non-crystalline fraction in ornithogenic soils (Table 5). A detailed study of the clay fraction in some ornithogenic sites is presented in Chapter 3.

According to Tatur and Barckzuk (1985), “phosphatization” comprises chemical transformation of rock minerals and release of amorphous Al and Fe minerals. These phases react with ornithogenic P, K and N to form amorphous and crystalline secondary phosphates. We have verified (see Chapter 3) that crystalline phosphates occur only in soils directly affected by penguins (active and abandoned rookeries). The incongruent dissolution of crystalline Al-Fe phosphates with formation of amorphous P-rich phases is considered the most common transformation with the increasing age of site abandonment (Tatur, 2002) and maintains high levels of labile P forms. On the other hand, at sites

Table 5 – Al, Fe and Si extracted with ammonium oxalate, Na-dithionite and Na-pyrophosphate.

Hor	**Depth**	**Si_{ox}[1]**	**Al_{ox}[1]**	**Fe_{ox}[1]**	**Fe_d[2]**	**Al_d[2]**	**Al_{pyr}[3]**	**Fe_{pyr}[3]**	**$(Al_{ox}-Al_{pyr})/Si_{ox}$**
	cm	**g/kg**							
Site 1 – pedon A10 - Typic Haploturbel/Turbic Cryosol									
C_1	0-10	32.0	25.0	3.6	-	-	0.4	0.0	-
C_2	10-20	22.0	19.0	3.3	17.2	1.6	0.0	0.0	0.9
Site 2 – pedon A9 - Lithic Haploturbel/Turbi-Leptic Cryosol									
A	0-10	-	11.4	20.5	23.9	7.1	2.0	2.0	-
C	10-20	-	14.4	-	-	-	2.3	0.2	-
Site 3 – pedon A4 - Typic Psammoturbel/Hapli-Turbic Cryosol									
O	0-10	2.8	13.2	17.2	-	-	7.6	5.8	2.0
A	10-20	1.2	16.3	24.6	-	-	9.9	7.7	5.2
Bi_1	20-30	2.7	15.6	18.8	18.1	9.9	8.1	6.8	2.8
BC	30-40	1.9	11.0	16.5	-	-	5.4	6.4	2.9
C	40-50	1.7	8.1	10.5	-	-	3.1	3.4	2.9
Site 4 – pedon A3 - Typic Psammoturbel/Skeleti-Turbic Cryosol									
A_1	0-10	2.0	8.2	13.4	-	-	-	-	-
A_2	10-20	1.9	7.9	13.9	-	-	-	-	-
Bi_1	20-30	1.8	10.5	12.6	13.0	8.3	-	-	-
Bi_2	30-40	1.6	14.4	12.4	-	-	9.3	3.4	3.1
BC	40-50	1.8	9.7	10.6	-	-	6.4	2.8	1.8
C_1	50-60	1.7	11.5	10.4	-	-	7.7	3.1	2.2
C_2	60-70	1.8	9.4	9.5	-	-	6.5	-	3.5
Site 5 – pedon A6 - Andic Umbriturbel/Umbri-Turbic Cryosol									
A_1	0-10	2.3	10.4	17.6	-	-	0.6	0.5	1.8
A_2	10-20	2.7	11.2	19.4	-	-	0.7	0.7	1.7
Bi	20-30	2.3	11.5	-	-	-	0.6	0.5	2.4
BC	30-40	1.8	11.4	18.2	-	-	0.6	0.4	2.9
C	50-60	1.4	9.5	19.0	-	-	0.8	0.3	1.1
Site 6 – pedon A1 - Andic Umbriturbel/Umbri-Turbic Cryosol									
$1A_1$	0-10	6.3	7.9	6.4	-	-	-	-	-
$1A_2$	10-20	5.3	7.4	6.3	-	-	-	-	-
$2Bi_1$	20-30	3.5	6.5	11.6	14.0	0.5	-	-	-
$2BC_1$	30-40	1.4	5.3	17.9	-	-	2.4	0.6	2.1
$2BC_2$	40-50	1.5	7.3	14.1	-	-	3.4	2.3	2.6
$2C_1$	50-60	1.8	8.3	10.4	-	-	3.9	2.3	2.5
Site 7 – pedon A5 - Andic Umbriturbel/Andi-Turbic Cryosol									
BC	20-30	3.0	8.6	12.4	-	-	6.6	7.3	0.7
Cox	30-40	0.9	8.7	15.0	23.2	10.7	10.7	4.8	-
Site 8 – pedon A2 - Psammentic Aquiturbel/Oxyaqui-Turbic Cryosol									
A	0-10	3.5	9.7	10.1	-	-	4.9	3.3	1.4
Bi_1	10-20	3.7	9.0	18.0	-	-	-	-	-
Bi_2	20-30	2.2	7.2	-	-	-	-	-	-
BC_1	30-40	1.9	8.4	20.4	-	-	-	-	-
C	40-50	2.1	8.6	22.2	-	-	-	-	-
Site 9 – pedon A7 - Terric Fibristel/Turbi-Histic Cryosol									
O_1	0-10	1.6	0.82	18.5	-	-	10.3	6.8	-
O_2	10-20	1.9	0.31	14.0	-	-	8.5	9.0	-
O_4	30-40	0.6	0.28	8.7	19.2	7.2	6.9	9.1	-
B_1	50-70	0.7	0.17	6.1	-	-	6.3	4.9	-
B_2	70-80	-	2.10	3.3	-	-	-	-	-
Site 10- pedon A8 - Lithic Umbriturbel/Gelic Fluvisols									
A	0-10	20.4	18.2	2.4	-	-	-	-	-
C_1	10-20	0.9	12.3	9.5	-	-	2.2	2.9	10.1
C_2	20-30	0.5	13.9	8.8	-	-	2.9	2.2	20.7

[1] Al, Fe and Si extracted with ammonium oxalate; [2] Al and Fe extracted with sodium dithionite; [3] organic matter bound Al and Fe extracted with sodium pyrophosphate; - not determined.

under indirect penguin influence (sites 6 and 8) P inputs are lower and no crystalline phosphates are present. Therefore, the chemical characteristics of these sites are controlled by highly reactive non-crystalline P minerals.

3.4 Micromorphology and microchemistry

The soils selected for OTM and SEM studies illustrate typical features observed in ornithogenic soils (sites 3 and 4). Both soils have accumulation of fibric organic residues at surface with abundant bryophytes and lichen talii, changing abruptly to a mineral phosphatic horizon of bleached colours. Medium-sized, sub-rounded, granular aggregates are present and include various pedogenic materials such as P-rich opaque organic remains and nodular P-rich features containing K, Al, Fe and Mg (Figure 2 and Table 6). The granular aggregates are usually encircled by secondary, pedogenic, illuvial P deposits of yellowish colours (Figure 2b and Table 6).

Little-altered rock fragments of diverse composition occur, with dominance of tuffs and basalts rich in magnetite, plagioclase and magnetite (not shown). Illuvial P is present as infillings along cleavage lines or cryoturbic fragments of rocks and aggregates (Figure 2b). Bone fragments are also common (Table 6).

The point analysis by energy dispersive spectrometry (SEM/EDS) revealed the chemical composition of several phosphate forms previously identified at OTM scale. At site 3, bone-apatite (P-Ca) fragments have 43.7 % of P_2O_5 and 52.9 % of CaO (Table 6). The P_2O_5 levels for illuvial features ranged from 1.4 to 4.8 %, with low CaO and K_2O and relatively high Al_2O_3 and SiO_2, indicating P reaction with amorphous Al-Si phases (Table 6). As mentioned previously in this paper, this reaction was expected due to the presence of allophane-like phases in the basaltic substrate prior to the occupation by penguins. Fe-rich phosphates are also present (Table 6) and show orange to reddish colours under the optical microscope (Figure 2). For Site 4, illuvial Al phosphate was present with low Fe, Si and K (Table 6). These data confirm the accumulation of secondary phosphates in these cryogenic soils due to intense P mobility and reaction with the mineral substrate.

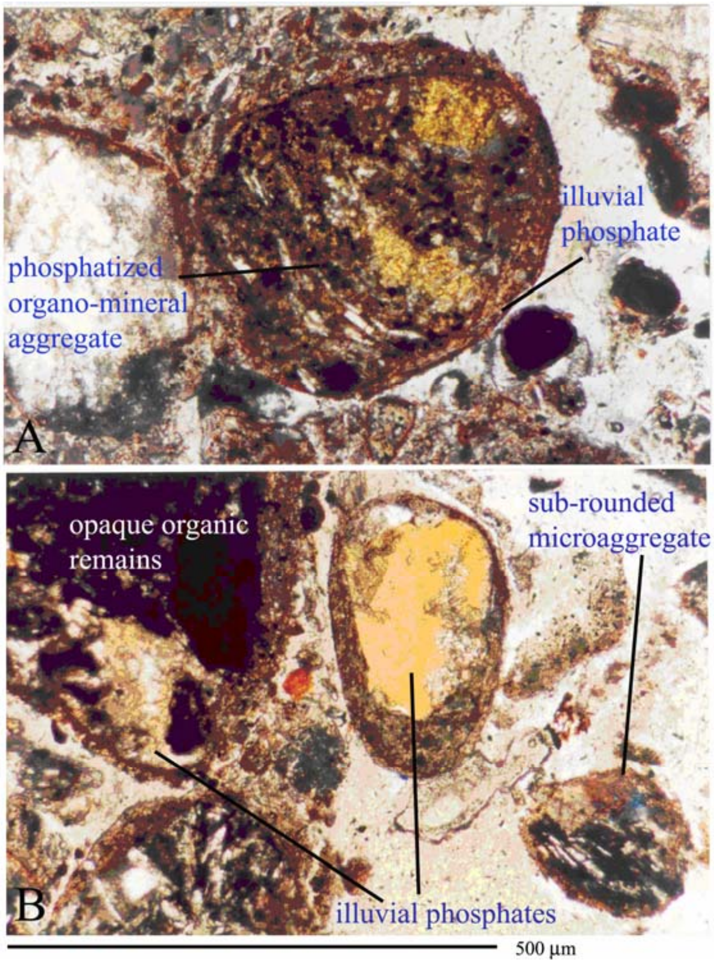

Figure 2 - Photomicrographs of the granular, sub-rounded structure in sites 3 (A) and 4 (B). (A) illustrates a highly phosphatized organo-mineral aggregate with yellowish illuvial phosphatic coating. (B) Opaque organic remains and phosphatic aggregates.

Table 6 – Microchemical analyses for some pedological features in sites 3 and 4 (means of three replicates).

Pedological feature	**P_2O_5**	**CaO**	**K_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**FeO**	**Total**
Site 3 – pedon A4	%							
Bone apatite	43.7	52.9	0.0	0.0	0.0	0.0	0.0	96.6
illuvial phosphate	4.8	0.6	0.4	13.3	16.5	38.0	18.3	91.8
Fe-phosphate	28.5	0.8	1.7	0.9	11.1	9.8	25.2	78.1
degraded K/Al phosphate	1.4	0.8	3.8	6.5	18.5	43.69	15.0	89.9
Site 4 – pedon A3								
Illuvial Al-phosphate	35.8	0.3	1.9	0.1	14.5	0.7	1.6	54.9

3.5 Classification of Ornithogenic Cryosols/Gelisols

Permafrost-affected soils are part of the Soil Taxonomy (SSSA, 2003) and *WRB* (ISSS Working Group RB, 1998) systems. At the moment, there is no qualifier in these systems for classification of bird-affected soils. Due to their unique pedogenetic evolution and distinct chemical, mineralogical, morphological and micromorphological characteristics we understand that the ornithogenic cryosols ought to be considered at a given level by soil classification systems as recently suggested by Michel et al., (2006).

We suggest the inclusion of the ornithogenic subgroup in all Suborders (Histels, Turbels and Orthels) of the Gelisol Order within the framework of Soil Taxonomy. We agree with the suggestion of Tarnocai et al., (2004) that third and fourth categorical levels should be included in the *WRB* system and we suggest the inclusion of the ornithogenic qualifier at the fourth categorical level.

Although further discussion is necessary for a more precise definition, we propose that ornithogenic soils of Antarctica should possess at least 3 of the following diagnostic criteria: (i) clear morphological evidences of bird activity (fresh droppings, nests, bone or eggshell remains); (ii) presence of light grey horizons and/or whitish coatings on rock surfaces; (iii) a provisory Melich-1 extractable-P > 500 mg/kg for the < 2 mm fraction; (iv) presence of crystalline or amorphous clay-sized phosphates.

In agreement with Tarnocai et al. (2004) studying the WRB classification, these provisory criteria for identification of the ornithogenic character need extensive field testing and evaluation.

A comparison between the current classification of soils from sites 1-10 and the classes proposed in the present paper is given in Table 7.

Table 7 – Actual and proposed classification for ornithogenic soils.

Soil Classification				
Site n^o	**Soil Taxonomy actual**	**Soil Taxonomy proposed**	**WRB actual**	**WRB proposed**
1	Typic Haploturbel	Typic Haploturbel	Turbic Cryosol	Eutric Turbic Cryosol
2	Lithic Haplorturbel	Lithic Haplorturbel	Turbi-Leptic Cryosol	Eutric Turbi-Leptic Cryosol
3	Typic Psammoturbel	Ornithogenic Psammoturbel	Hapli-Turbic Cryosol	Dystric Hapli-Turbic Cryosol (ornihthogenic)
4	Typic Psammoturbel	Ornithogenic Psammoturbel	Skeleti-Turbic Cryosol	Dystric Skeleti-Turbic Cryosol (ornithogenic)
5	Andic Umbriturbel	Ornithogenic Umbriturbel	Umbri-Turbic Cryosol	Dystric Umbri-Turbic Cryosol (ornithogenic)
6	Andic Umbriturbel	Ornithogenic Umbriturbel	Umbri-Turbic Cryosol	Eutric Umbri-Turbic Cryosol (ornithogenic)
7	Typic Haploturbel	Ornithogenic Haploturbel	Andi-Turbic Cryosol	Dystric Andi-Turbic Cryosol (ornithogenic)
8	Psammentic Aquiturbel	Ornithogenic Aquiturbel	Oxyaqui-Turbic Cryosol	Dystric Oxyaqui-Turbic Cryosol (ormithogenic)
9	Terric Fibristel	Ornithogenic Fibristel	Turbi-Histic Cryosol	Dystric Turbi-Histic Cryosol (ornihthogenic)
10	Andic Cryofluvent	Ornithigenic Cryofluvent	Gelic Fluvisols	Dystric Gelic Fluvisols (ornithogenic)

4. Conclusions

1. At upland sites with no vegetation or ornithogenic influence, soil chemistry and mineralogy are related mainly to the physical weathering of the basaltic till. The ornithogenic influence alters site characteristics leading to soil acidification, leaching of exchangeable bases, transformation of primary minerals and release of amorphous Fe and Al. These phases react with the ornithogenic P, characterizing the phosphatization process. This is the main soil forming process at these sites and results in a predominantly phosphatic fine fraction and an impressive increase of soil P pool, with very high levels of labile and moderately labile P forms.

2. Higher P and N levels at ornithogenic sites favour vegetation establishment with presence of *Deschampsia antarctica* and *Colobanthus quitensis*. High organic carbon contents characterise ornithogenic sites as important C sinks at Antarctic terrestrial ecosystems.

3. Ornithogenic sites control sea-land P fluxes on ice-free areas of Maritime Antarctica. P is temporary immobilized in soils as crystalline and non-crystalline Al/Fe phosphates and partially drained back into the shallow sea by melting waters draining ornithogenic areas. Crystalline Al and Fe phosphates persist in soils even after site abandonment by penguins and act as P reserves.

3. The degree of ornithogenic influence can be assessed through the analysis of soils morphological, chemical and mineralogical characteristics. The study of these characteristics allowed the proposal of provisory diagnostic criteria for the *ornhithogenic* qualifier, providing a better classification of these unique soils within the WRB and Soil Taxonomy systems.

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CAPÍTULO 3

Clay-sized minerals in ornithogenic Cryosols from Admiralty Bay, King George Island, Antarctica

Abstract

Cryosols from Maritime Antarctica have been less studied than soils from continental areas of Antarctica. In this work XRD, DXRD, DTA/TG, TEM/EDS and selective chemical dissolution were used to characterize the clay fraction of basaltic, acid sulphate and ornithogenic cryosols from ice-free areas of Admiralty Bay, King George Island. Randomly interstratified smectite-hydroxyl-Al-interlayered smectite is the main clay mineral of basaltic soils. Kaolinite, chlorite and regularly interstratified illite-smectite predominate in acid sulphate soils. Jarosite is also an important component of the clay fraction in theses soils. Crystalline Al and Fe phosphates occur in the clay at sites directly affected by penguin activity and the chemical characteristics of these ornithogenic sites are controlled by highly reactive Al, Si, Fe and P phases. Chemical weathering is an active process in cryosols in Maritime Antarctica and is enhanced by the presence of sulphides for some parent materials, and faunal activity.

Keywords – allophane, amorphous minerals, clay minerals, Cryosols, Maritime Antarctica, ornithogenesis, phosphate, soils.

1. Introduction

Most pedological studies in Antarctica have dealt with soils from extremely cold and dry continental areas where physical weathering accounts for the rather incipient soil development (Kelly and Zumberge, 1961; Campbell and Claridge, 1987, 2004a, 2004b; Bockheim and Tarnocai, 1998). Soils from Maritime Antarctica have received much less attention. In this part of Antarctica, warmer temperatures, higher liquid water availability, widespread presence of bird colonies, pronounced vegetation development and higher soil microbial activity result in more developed soils.

Some authors have stated that under these conditions chemical weathering is an important soil forming process leading to considerable amounts of pedogenic iron oxides, phosphates and clay minerals (Tatur and Barczvk, 1985; Tatur, 1989; Blume *et al.*, 2002; Blume *et al.*, 2004). Other authors concluded that even under maritime conditions chemical weathering is insignificant and have attributed the formation of clay minerals to hydrothermal alteration of parent materials and eolian inputs from nearby active volcanoes (Jeong and Yoon, 2001; Yong *et al.*, 2004). Clearly our understanding of soil formation in Maritime Antarctica is still limited.

Due to their large specific area, clay-sized minerals greatly influence soil physical and chemical properties, even when they are present in small amounts. Various environmental issues, such as the influence of acid deposition on soils, retention and cycling of organic and inorganic contaminants, nutrient availability and organic C dynamics, are strongly related to the clay formation. This is of particular importance in Antarctica where there is increasing impact of local and global human activities on these fragile ecosystems. In this paper, we have studied in detail the clay fraction from the main soil types at Admiralty Bay, King George Island.

2. Material and Methods

2.1 Study area

Admiralty Bay (62^{o}03’40”-62^{o}05’40” S and 58^{o}23’30”-58^{o}24’30” W) is located in King George Island and is part of the South Shetlands Archipelago, Maritime Antartica (Figure 1). Data sets from 1982-2002, acquired at the Brazilian Comandante Ferraz Station, report mean air temperatures varying from -6.4 ^{o}C in July to + 2.3 ^{o}C in February. Mean annual precipitation is 366.7 mm. Positive air temperatures occur from November until March when effective precipitation as liquid water is increased due to melting of accumulated winter snow. Soils have formed predominantly from tholeite basalts and, to a lesser extent, from sulphide-bearing andesites and related moraine, solifluction and fluvioglacial deposits. Intense paleohydrothermal activity (Yong et al., 2004) and recent eolian deposition of volcanic ash in this part of Antarctica have been reported (Blume et al., 2004; Yong et al., 2004).

2.2 Site characteristics and soil sample treatments

We have selected two altitudinal sequences ranging from upland, ahumic soils to lower, acid, ornithogenic soils with higher organic C contents, as well as acid soils formed from sulphide bearing rocks and related deposits. Soil pH, nutrient availability, exchangeable Al and particle size distribution were determined for < 2 mm samples (EMBRAPA, 1997). Total organic C was determined on < 0.5 mm samples by wet combustion (Yeomans and Bremner, 1988). General site descriptions and their approximate location are presented in Table 1 and Figure 1, respectively. Some important chemical and physical characteristics of the soils are presented in Table 2. The clay fraction was separated by dispersion in pH 10.0 water (1 g Na_2CO_3 : 10 L of deionized water), sieving of the sand fraction and sedimentation of silt + clay followed by siphoning of the < 2 µm fraction (Gee and Bauder, 1986).

Based on their general chemical properties, which are greatly influenced by parent materials and bird detritus, the soils are grouped as follows:

Group 1. Basaltic soils - Sites 1 and 2

Group 2. Ornithogenic soils - Sites 3, 4, 5, 6 and 7

Group 3. Acid sulphate soils - Sites 8 and 9

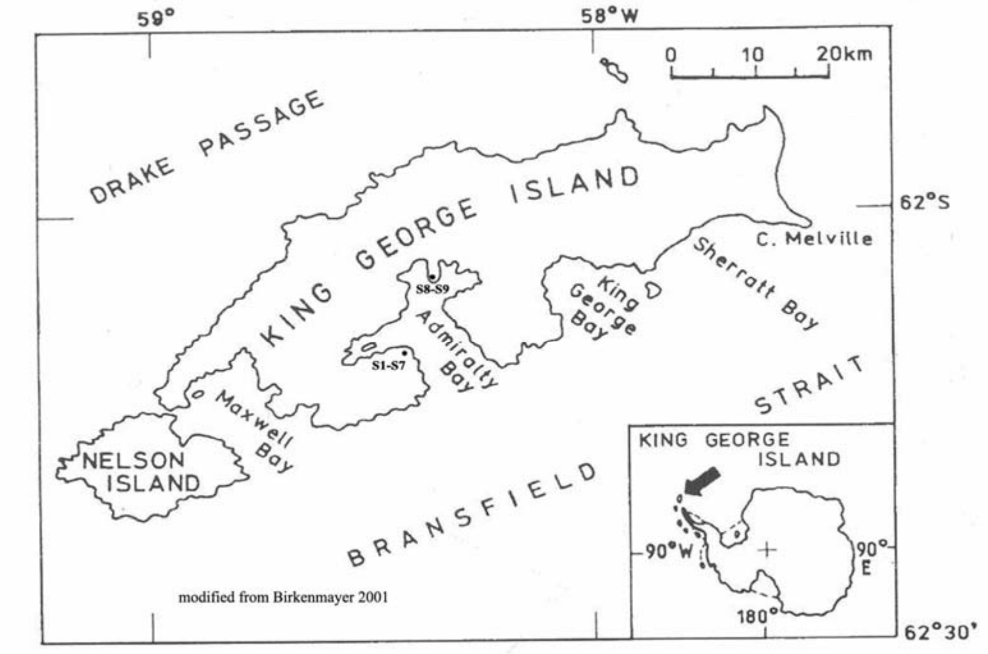

Figure 1 –King George Island and the location of the studied sites at Admiralty Bay (S1-S9).

Table 1 - General characteristics of the studied sites.

Site and pedon	Altitude[1]	Vegetation[2]	Description
Group 1 – Basaltic soils			
Site 1- pedon A10	147	Absent	Subpolar desert without any ornithogenic influence and absence of vegetation.
Site 2 – pedon C4	90	U	Well drained, no ornithogenic influence, sparse vegetation.
Group 2 – Ornithogenic soils			
Site 3 – pedon A4	72	D > C	Abandoned penguin rookery on the highest level of ornithogenic influence; probably the most ancient level of ornithogenic soils; well developed, continuous vegetation. Permafrost at 50 cm.
Site 4 – pedon A3	69	D > M > C	Abandoned well drained penguin rookery; phosphatization evidenced by whitish discontinuous horizons throughout the profile; well developed, continuous vegetation. Permafrost at 50 cm.
Site 5 – pedon A2	32	M > D	Poorly drained. This site receives a high amount of leachate from the upslope ancient rookeries; well developed continuous vegetation.
Site 6 – pedon C1	63	M>D>U>C	Well drained. Indirect ornithogenic influence through lateral leacheate. Exuberant vegetation cover. Abundant roots down to 25 cm. Fibric O horizon from 0-10 cm.
Site 7 – pedon C2	61	M>D>U>C	Well drained, similar to site 6. Buried O horizon at 30-40 cm.
Group 3 -Acid sulphate soils			
Site 8 – pedon K7	69	Rare crustose lichens	Shallow profile, lithic contact at 35 cm. Basaltic colluvium overlying yellowish, acidic material.
Site 9 – pedon K24	47	U>M>D	Stable terminal moraine. Whole profile affected by sulphates. Representative of soils formed from sulphide-affected rocks of Keller Peninsula. Permafrost at 40 cm.

[1] meters above sea level.[2] D- *Deschampsia Antarctica* (Gramineae); C – *Colobanthus quietensis* (Cariofilaceae); M – mosses; U – *Usnea sp.* (lichen);

Table 2 - Some chemical and physical characteristics of the studied soils.

Depth	pH$^{/1}$	P$^{/2}$	Al$^{/3}$	TOC$^{/5}$	csand	fsand	silt	clay
cm		mg/kg	cmo$_c$/dm^3	g/kg	dg/kg			
Site 1 – pedon A10								
0-20	6.8 (0.3)	56.6 (11.9)	0.3 (0.2)	1.0	49.5	21.0	25.0	15.0
Site 2 – pedon C4								
0-50	7.1 (0.7)	516.5 (58.5)	0.2 (0.2)	3.2 (4.3)	33.0	8.6	35.6	22.8
Site 3 –pedon A4								
10-50	4.2 (0.1)	1015.3 (267.4)	10.5 (2.5)	6.0 (2.7)	59.2	13.4	19	8.5
Site 4 – pedon A3								
0-70	4.1 (0.3)	1421.8 (310.3)	6.2 (1.5)	13.0 (2.3)	80.5	5.0	7.5	7.0
Site 5 - pedon A2								
0-40	5.1 (0.5)	391.0 (102.0)	6.2 (3.3)	20.5 (18.6)	73.6	5.3	8.1	24.3
40-50	4.9	826.2	3.3	8.0	74.0	6.4	11.8	10.2
Site 6 – pedon C1								
10-40	4.0 (0.1)	1049.9 (55.7)	6.5 (0.7)	32.7 (6.1)	50.0	16.3	25.7	8.0
Site 7 – pedon C2								
0-20	4.5 (0.1)	726.9 (14.0)	3.9 (0.5)	66.0 (16.9)	72.0	3.0	14.0	11.0
20-40	4.3 (0.1)	1140.1 (238.0)	5.0 (0.7)	100.0 (9.9)	68.0	8.0	14.0	10.0
Site 8 – pedon K7								
0-10	7.6	173.5	0.0	4.0	29.0	8.0	34.0	29.0
20-30	4.7 (0.2)	36.7 (13.8)	17.1 (1.2)	1.0	20.0	6.0	72.0	2.0
Site 9 – pedon K24								
0-10	5.1	44.6	7.6	5.0	52.0	6.0	26.0	16.0
20-70	4.5 (0.3)	21.3 (4.0)	27.7 (7.3)	1.2 (0.4)	29.2	7.2	64.0	1.0

2.3 Chemical dissolution

The use of selective dissolution for mineralogical studies is well reported in the literature (Campbell and Schwertmann, 1985; Smith, 1994; Melo *et al.*, 2002a). In this study natural (untreated) clay samples were submitted to the following sequential extraction:

(i) pH 10.0 Na-pyrophosphate (pyr) - extraction of Al and Fe bound to organic matter (Dahlgren, 1994);

(ii) pH 3.0 0.2 mol/L ammonium oxalate in the dark (ox)- extraction of poorly ordered Fe, Al and Si compounds (Schwertmann, 1973);

(iii) 0.5 mol/L NaOH (OH) - extraction of poorly ordered aluminosilicates not removed by the previous extractions (Jackson *et al*., 1986, modified by Melo *et al*., 2002a, 2002b).

The general procedure for all extractions was: a) drying of the samples at 105 °C for 12 hours before and after each extraction to obtain initial and final weights to 0.0001g; b) removal of excess salt by washing with 0.5 M $(NH_4)_2CO_3$ and deionized water after each extraction; c) Al, Fe, Si, Mg and Ca in the extracts were determined by Ignited Coupled Plasma (ICP) and results converted to percentage oxides. P concentration was determined in the oxalate and NaOH extracts by photocolorimetry and is expressed as P_2O_5. The total mass removed by each treatment for an initial mass of 1000 g is as follows:

$T_i = Y_i + X_i + Z_i$ where:

T_i = Total mass removal for sample i (g/kg);

Y_i = removal by pyrophosphate extraction (g/kg);

X_i = (0,001*removal by oxalate extraction (g/kg))*(1000-Yi);

Z_i= (0,001*removal by NaOH extraction (g/kg))*(1000-(Xi+Yi)).

2.4 X-Ray diffraction (XRD) and differecence XRD (DXRD)

Aproximately 0.5 g of finely ground dry clay samples were mounted on aluminium holders and submitted to XRD analysis. XRD patterns samples were obtained before and after each extraction, following the procedure proposed by Schulze (1994). Difference XRD (DXRD) patterns were obtained by subtracting the pattern for a treated sample from the XRD pattern obtained prior to the treatment (Untreated sample - pyr, pyr-ox and ox-OH) (Campbell and Schwertman, 1985; Schulze, 1994).

Oriented clays on ceramic plates were analyzed by XRD after Mg saturation, liquid glycerol solvation and K saturation (room temperature, heating at 400 ^oC and 550 ^oC for 1 hour). In order to resolve kaolinite and chlorite peaks for Group 3 clays, oxalate-extracted, dry clay samples were ground with 20 % of urea (in weight) as described in Gardolinki *et* *al*., 2001.

Random powder samples of the finely ground sand fraction from some sites were also analyzed by XRD. All XRD patterns were obtained using monochromated CuKα radiation and were interpreted according to Brindley and Brown (1980) and Nriagu and Moore (1984).

2.5 Difference thermal (DTA) and thermogravimetric (TG) analyses

Simultaneous DTA and TG analyses of the oxalate treated samples were carried out using a Shimadzu DTG-60 instrument by heating 20 mg of sample from ambient temperature to 1000 ºC at 10 °C min^{-1}, under N_2-atmosphere. In this paper, only data from Group 3 sites are presented. Using the TG results, the amount of kaolinite in clay samples from Sites 8 and 9 was estimated according to Jackson (1979) and Tan *et al*. (1986).

2.6 Transmission electron microscopy (TEM) and energy dispersive spectrometry (EDS)

Dilute clay suspensions were mounted on carbon coated copper grids and analyzed using a JEOL 3000F field emission gun TEM (FEG-TEM) equipped with an Oxford Instruments INCA 200 EDS system. All images, EDS analyses and electron diffraction patterns were acquired at 300 kV accelerating voltage.

3. Results and Discussion

3.1 Group 1- Basaltic ahumic soils (sites 1 and 2)

The XRD results indicate that the sand fraction (data not shown) of these soils consists mainly of plagioclases (major reflections at 3.21 Å, 3.19 Å and 2.16 Å), with minor amounts of pyroxene (3.12 and 2.88 Å), magnetite (2.53, 2.44, 2.10, 1.61 Å) and traces of quartz (3.33 Å). A weak peak at 15.0 Å indicates the presence of smectite in the sand fraction. Plagioclase, quartz, pyroxene and magnetite are also common in the clay fraction as confirmed by TEM/EDS analyses (Figure 2).

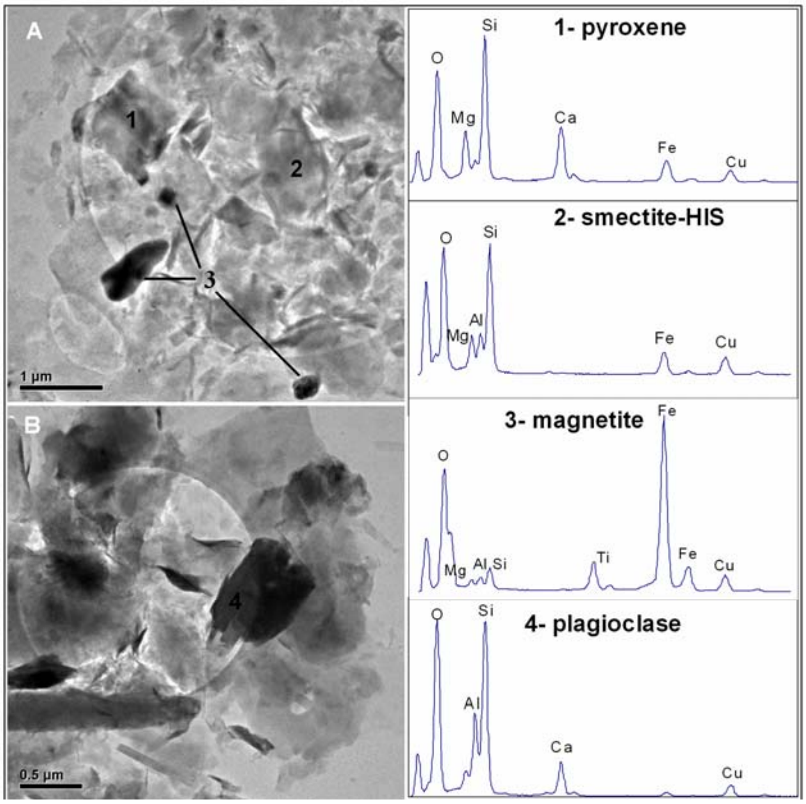

Figure 2 – TEM images and qualitative EDS analyses of the clay fraction from Site 1: A) 1-pyroxene; 2- interstratified smectite-HIS , 3- magnetite and; B) 4- plagioclase. Cu peaks in the EDS spectra are due to interference from the copper grid.

Smectites are present in the XRD patterns for both sites as indicated by the sharp peak at 14.3-14.5 Å for the Mg-saturated sample (Figure 3), expanding to 16.5-16.6 Å after glycerol solvation (Figure 4 – A and C). The 060 reflection at 1.50 Å (not shown) indicates the dioctahedral nature of this clay mineral (Borchardt, 1989; Egli *et al*., 2001).

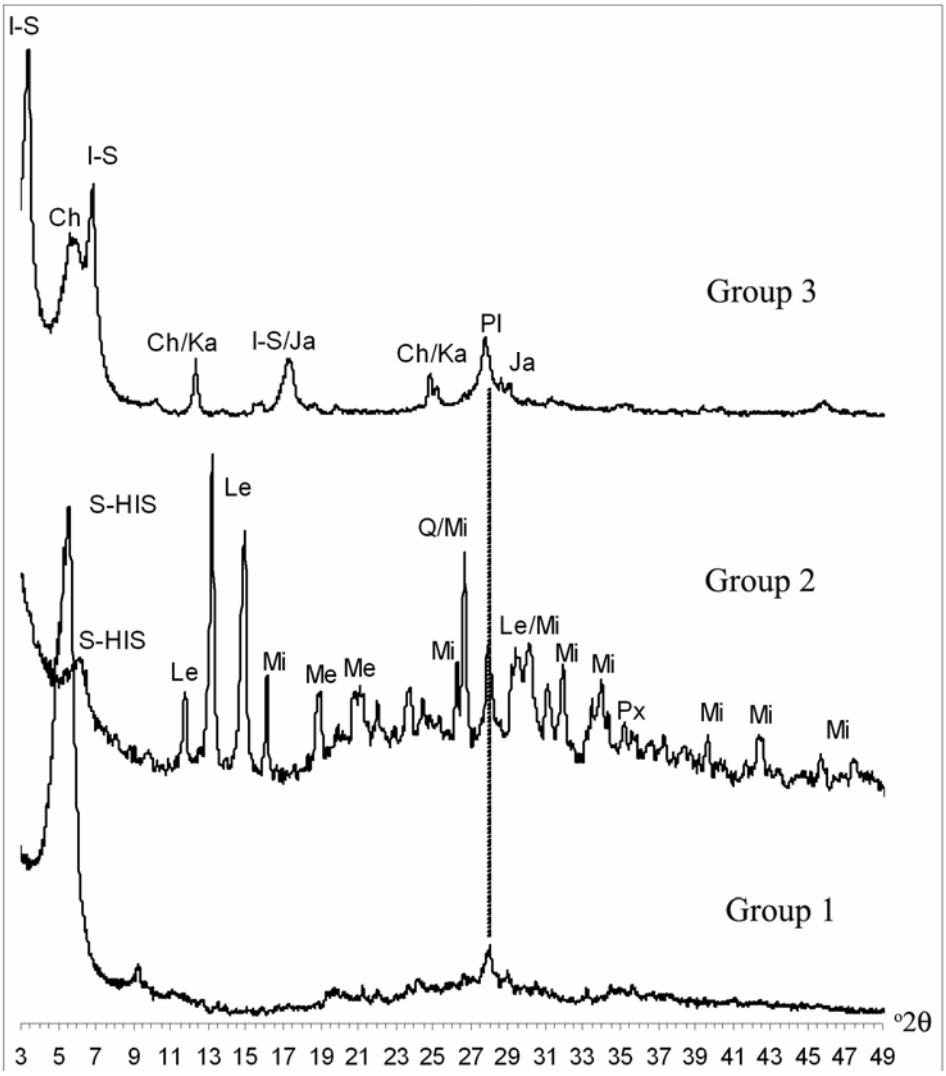

Figure 3 – Representative XRD patterns of basally oriented Mg-saturated clays from each soil group. (I-S – interstratified illite-smectite; Ch – chlorite; Ka – kaolinite; Ja – jarosite; S-HIS – interstratified smectite-hydroxyl-Al-smectite; Le – leucophosphite; Mi – minyulite; Me – metavariscite; Pl – plagioclase; Q – quartz; Px – pyroxene).

For Site 1, the K-saturated sample had a peak at 12.7 Å, shifting after heating at 550 °C to a broad peak with two maxima at 12.3 Å and 10.5 Å (Figure 4 – A). For Site 2, a broad asymmetrical peak with maxima at 13.9 Å and 12.4 Å was formed after K saturation, shifting after heating to an asymmetrical peak at 10.3 Å with a broadening towards higher d values (Figure 4-C).

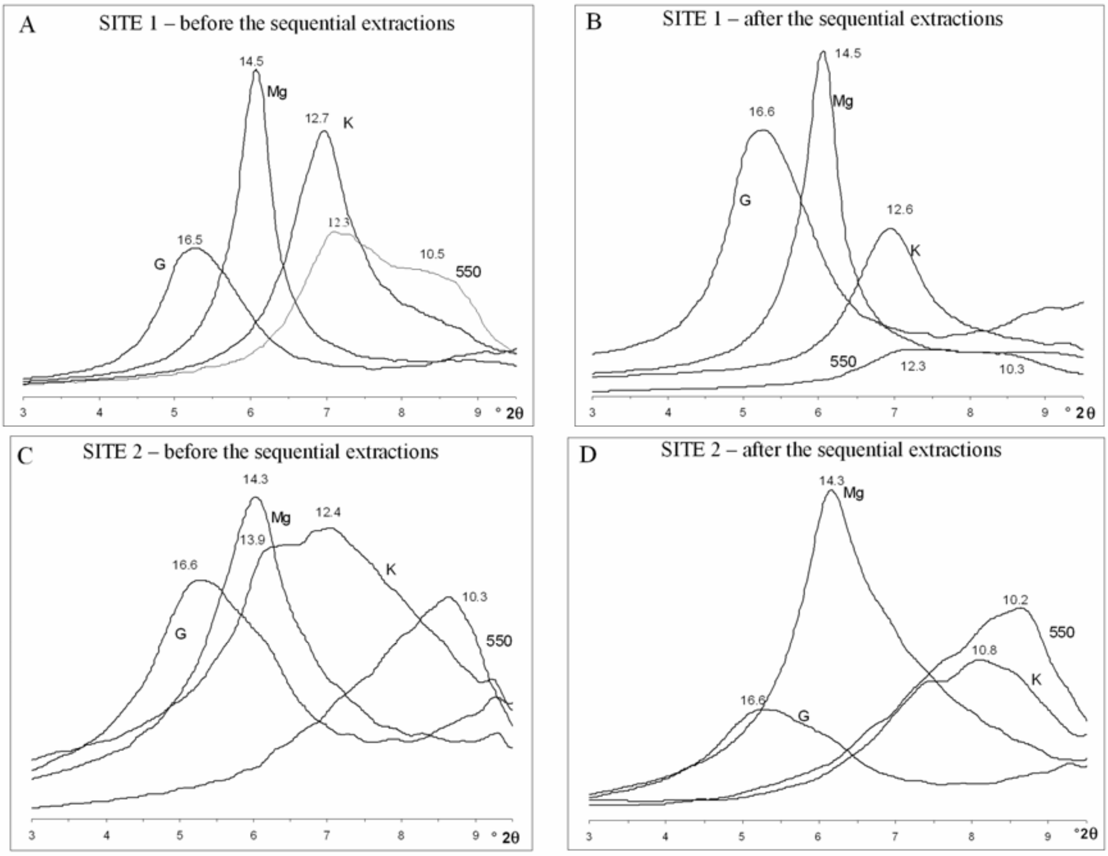

Figure 4 – XRD patterns of oriented clay before (A and C) and after (B and D) the sequential pyrophosphate-oxalate-NaOH extractions showing shifts of the 001 reflection (Å) of the S-HIS mineral for Sites 1 and 2 after the following treatments: G – glycerol solvation; Mg –saturation with $MgCl_2$; K-saturation with KCl at room temperature; 550 – heating at 550 °C of K saturated clay.

The resistance of the K-saturated mineral to collapse to 10.0 Å even after heating at 550 ^{o}C suggests the presence of hydroxyl-Al interlayers (Barnhisel and Bertsch, 1989), characterizing a randomly interstratified smectite-hydroxy-Al smectite (S-HIS). The peak positions after K saturation or glycerol solvation depend on the proportion of each phase in the interstratified mineral (Sawhney, 1989). Higher proportions of HIS layers result in peaks closer to 14.4 Å. Therefore, the results suggest relatively higher proportions of HIS layers for Site 2 since part of the layers kept a 13.9 Å *d* value after K saturation.

It is also known that more stable interlayer constituents require higher temperatures to produce shifts to lower d values for K-saturated clays (Barnhisel and Bertsch, 1989). In the present study, the interlayer component in clays from Site 2 was more easily removed by heating and by chemical extractions than in Site 1 (Figures 4 C and 4 D). The lower stability of the hydroxyl-Al component and/or lower degree of interlayer filling for Site 2 is suggested by the lower d value obtained after heating at 550 ^{o}C in relation to Site 1 (Figure 4 A and C). For the extracted sample (Figure 4 D), a broad peak with clear maximum at 10.8 Å was formed after K saturation shifting to 10.2 Å after heating. This indicates that most of the hydroxyl-Al interlayers were effectively removed by the sequential extraction. On the other hand, the chemical extractions had little effect on the Site 1 sample, indicating the higher stability of the interlayer components.

We found no evidences of neoformation of smectites in soils from Admiralty Bay. The presence of clay-sized pyroxene and plagioclase indicate a very low degree of chemical alteration of the parent material. Jeong and Yoon (2001) and Yong *et al*. (2004) consider that smectites in King George Island soils are likely to have been inherited from bedrock hydrothermal alteration. The presence of smectite in the sand fraction of Group 1 soils also indicates that the clay fraction may be at least partially inherited through cryoclastic weathering of coarser soil particles.

Once in the soil environment, the polymerization of hydroxyl-Al in the interlayer spaces of smectites is expected even under weak weathering conditions (Borchardt, 1989). The acid attack of both tetrahedral and octahedral sheets of the expansible mineral and the weathering of aluminous minerals such as plagioclases are possible sources of hydroxyl-Al polymers (Wilson, 1999).

Approximately 25 (± 0.4) % of the clay fraction was removed by the chemical extractions for Site 1 and 14 (± 1.4) % for Site 2 (*i.e.* TMR - Table 3). As the Na-pyrophosphate and ammonium oxalate extractions are assumed to have had no effect on crystalline minerals, the total mass removal (TMR) by these extractions provides an estimate of the non-crystalline components in the clay fraction. For Sites 1 and 2, the non-crystalline phases account for 16 (± 0.8) % and 8 (± 1.2) % of the clay fraction, respectively (Table 3). The oxalate extraction accounted for 80 % of these amounts, indicating that amorphous allophane-like minerals were the main extracted phase.

The DXRD patterns obtained after the oxalate extraction (pyr-ox) resemble those described for allophane, with broad maxima at 3.3 and 2.2 Å (Campbell and Schwertmann, 1985; Wada, 1989; Parfitt, 1990). The Al/Si ratio in the oxalate extracts for both sites is close to 1.0 (Table 4), which is similar to Si-rich allophanic materials described by Parfitt (1990). Pumice allophane (Farmer *et al*., 1979), defect kaolin allophane (Parfitt and Wilson, 1985) and halloysite-like allophane (Yoshinaga, 1986) are names which have been proposed for Si-rich allophanes (Parfitt, 1990). The amount of amorphous allophane-like phases is obtained by multiplying the % Si in the oxalate extract by 5 (Parfitt, 1990; Smith, 1994). Approximately 14 % and 6 % of the clay from Sites 1 and 2, respectively, is composed of a Si-rich allophane-like phase(s).

Table 3 – Sequential extraction data for the clay samples

Depth	Pyrophosphate			NH$_4$-Oxalate				NaOH[/1]			Mass removal[/2]				
	Al_2O_3	Fe_2O_3	SiO_2	Al_2O_3	Fe_2O_3	SiO_2	P_2O_5	Al_2O_3	SiO_2	P_2O_5	TMR	Pyr	Ox	NaOH	Pyr + Ox
cm	g/kg										%				
SITE 1 – pedon A10															
0-10	5.2	1.0	0.0	31.8	7.7	30.2	7.2	11.6	6.2	0.8	24.9	3.6	12.1	9.2	15.7
10-20	5.5	0.7	0.2	27.0	7.1	34.2	6.8	6.3	5.2	0.5	24.3	3.7	13.1	7.5	16.8
SITE 2 – pedon C4															
0-10	3.5	2.2	3.7	9.4	6.9	11.2	6.8	3.9	3.5	0.4	20.6	2.6	5.7	7.9	8.3
10-20	2.1	1.9	1.7	10.5	6.7	14.0	5.9	3.3	3.1	0.4	18.7	2.7	5.4	5.9	8.1
20-30	1.5	0.7	1.0	10.1	6.0	15.6	5.9	3.4	3.2	0.5	23.5	0.4	5.4	7.1	5.8
30-40	1.8	1.4	1.2	9.9	6.6	11.5	5.7	2.6	2.7	0.5	23.7	1.1	7.5	7.1	8.7
40-50	2.0	1.3	2.2	8.7	5.6	11.4	4.9	2.9	2.6	0.6	26.3	1.6	4.6	7.0	6.2
50-60	1.7	0.9	1.7	10.2	6.2	13.3	5.6	3.3	2.7	0.4	20.6	0.6	5.9	7.2	6.5
SITE 3 – pedon A4															
10-20	40.3	24.7	3.5	25.2	18.7	13.0	43.4	3.8	5.5	0.4	48.1	27.7	10.7	9.7	38.4
20-30	38.6	22.6	5.3	29.0	38.4	9.3	69.3	2.9	4.8	0.3	52.7	27.2	17.2	8.3	44.4
30-40	24.2	17.2	3.2	35.1	41.7	8.4	74.7	5.4	5.6	1.1	53.3	17.9	23.6	11.8	41.5
40-50	24.5	21.8	3.9	31.7	24.4	6.7	53.2	19.7	13.7	28.9	60.0	16.1	19.2	24.7	35.3
SITE 4 – pedon A3															
0-10	30.7	20.7	1.5	16.1	11.3	7.6	9.6	8.4	13.3	5.4	44.2	21.0	7.4	15.8	28.4
10-20	52.2	41.3	2.5	26.8	14.9	9.4	20.5	12.1	19.7	4.7	67.1	39.5	10.1	17.5	49.6
20-30	78.4	28.8	5.0	33.1	15.6	5.7	31.7	71.0	8.6	102.0	82.8	46.2	11.7	24.8	57.9
30-40	65.7	18.2	1.7	30.3	14.1	4.3	33.2	94.5	7.9	135.1	81.6	32.2	12.9	36.6	45.1
40-50	58.0	21.9	2.3	29.2	15.4	7.7	28.3	62.0	17.3	87.5	70.3	29.0	13.6	27.6	42.6
50-60	58.1	20.9	2.1	30.7	16.5	4.6	32.4	81.6	13.1	112.3	78.0	27.7	13.7	36.6	41.4
60-70	66.1	26.8	5.8	36.4	17.1	5.6	36.6	80.1	14.4	111.9	81.6	37.8	13.9	30.0	51.7
SITE 5 – pedon A2															
0-10	20.9	15.2	2.1	16.6	11.0	11.7	5.7	5.2	9.7	0.7	38.0	20.6	7.9	9.5	28.5
10-20	25.1	22.0	1.4	16.4	13.6	9.2	7.3	6.0	9.8	1.1	38.6	18.7	8.7	11.2	27.4
20-30	26.1	29.1	6.2	13.2	16.6	5.9	8.8	6.5	8.8	1.6	38.3	23.5	7.0	7.8	30.5
30-40	32.0	35.2	10.9	13.2	15.7	5.7	8.2	7.1	8.3	1.0	36.5	23.7	7.0	5.8	30.7
40-50	38.5	33.0	11.3	13.6	15.5	5.7	9.1	6.1	8.1	1.0	42.9	26.3	8.8	7.7	35.2
SITE 6 – pedon C1															
10-20	18.5	20.8	4.0	12.9	9.6	7.6	15.1	3.7	8.8	1.4	62.8	26.2	21.2	15.3	47.4
20-30	23.6	26.5	2.5	19.3	15.3	9.0	18.6	4.0	10.2	0.8	46.9	24.6	9.5	12.8	34.1
30-40	36.4	39.8	3.9	16.3	12.5	8.5	13.9	4.0	10.3	0.9	52.7	31.7	8.0	13.0	39.7
SITE 7 – pedon C2															
10-20	26.4	28.7	1.8	12.2	10.0	8.1	10.5	4.3	9.0	1.4	51.5	30.2	7.1	14.3	37.3
20-30	16.8	22.9	1.4	10.8	9.1	5.7	10.5	3.8	8.6	1.2	51.0	31.5	6.4	13.0	38.0
30-40	88.3	61.5	2.0	10.5	6.8	6.2	6.6	3.5	8.6	1.2	67.7	52.8	4.0	11.0	56.7
40-50	38.5	28.9	2.0	13.9	14.0	7.1	15.7	3.9	5.9	3.2	59.5	41.7	6.5	11.3	48.2
SITE 8 – pedon K7															
0-10	1.9	0.6	0.0	2.8	6.0	0.5	1.0	3.0	8.2	0.4	14.7	8.7	3.7	2.3	12.4
10-20	5.3	1.4	1.9	3.1	15.8	0.6	4.3	2.1	6.7	1.1	21.3	14.1	5.0	2.2	19.1
20-30	7.0	1.6	3.9	2.9	14.1	0.6	3.7	1.6	5.8	0.7	22.8	13.7	6.0	3.2	19.6
SITE 9 – pedon K24															
0-10	6.8	2.0	6.8	7.3	15.7	4.5	5.6	3.9	1.5	0.9	20.1	3.5	8.2	8.5	11.7
10-20	5.0	1.5	4.7	6.9	20.5	3.9	6.0	3.3	1.3	1.0	21.1	1.9	8.5	10.7	10.4
20-30	22.8	6.3	26.9	4.2	21.3	2.0	8.2	3.0	1.5	1.1	26.0	7.2	9.3	9.5	16.5
30-40	26.5	7.2	32.8	3.9	22.0	1.8	8.4	2.5	1.3	1.1	27.4	8.5	9.3	9.6	17.8
40-50	11.0	4.2	10.8	4.7	23.4	1.3	5.8	3.2	1.4	1.0	21.8	6.1	6.5	9.2	12.6
50-60	14.9	4.4	15.1	3.8	21.2	1.9	5.4	3.6	1.5	1.1	24.6	10.1	5.8	8.7	15.9

[/1] Fe_2O_3 levels in the NaOH extracts < detection limit and therefore are not presented; [/2] % of mass removal from the clay fraction by each extractant: TMR- total mass removed; Pyr = Na-Pyrophosphate extraction; Ox = NH$_4$-Oxalate extraction.

Table 4 – Mean values and standard errors ( ) of Al/Si and $P_2O_5/(Al_2O_3 + Fe_2O_3)$ ratios for oxalate extracts of the clay fractions.

Depth (cm)	**Alo/Sio**	**$P_2O_5/(Al_2O_3 + Fe_2O_3)$**
SITE 1 – pedon A10		
0-20	0.9 (0.1)	0.2 (0.0)
SITE 2 – pedon C4		
0-60	2.0 (0.4)	0.4 (0.0)
SITE 3 – pedon A4		
10-20	1.9	1.0
20-50	4.0 (0.8)	1.0 (0.1)
SITE 4 – pedon A3		
0-20	2.5 (0.4)	0.4 (0.1)
20-70	6.0 (1.3)	0.7 (0.0)
SITE 5 – pedon A2		
0-50	2.0 (0.4)	0.3 (0.0)
SITE 6 – pedon C1		
10-40	1.9 (0.2)	0.6 (0.1)
SITE 7 – pedon C2		
10-50	1.8 (0.2)	0.5 (0.1)
SITE 8 – pedon K7		
0-10	5.1	0.1
10-30	5.3 (0.3)	0.2 (0.0)
SITE 9 – pedon K24		
0-60	2.2 (0.7)	0.3 (0.1)

3.2 Group 2- Ornithogenic soils (Sites 3, 4, 5, 6 and 7)

Similarly to Group 1 soils, the interstratified S-HIS is the dominant crystalline clay mineral in the clay fraction of Group 2 soils (Figure 3). Similar peaks before and after the chemical extractions for all clay treatments suggest that little interlayer component was removed. All soils of Group 2 also contain small amounts of quartz, plagioclase, and Fe-Ti oxides in the clay fraction as confirmed by TEM/EDS analysis (Figure 5). Apart from this similarity in clay mineralogy, the XRD patterns indicate that there are pronounced mineralogical differences from Group 1 soils for those sites directly (3 and 4) or indirectly influenced by penguin activity (sites 5, 6 and 7). For the former sites sharp, intense peaks of several crystalline phosphates occur which are listed in Table 5 and illustrated in Figure 3.

These minerals were present only in layers deeper than 20 cm at both sites (3 and 4).

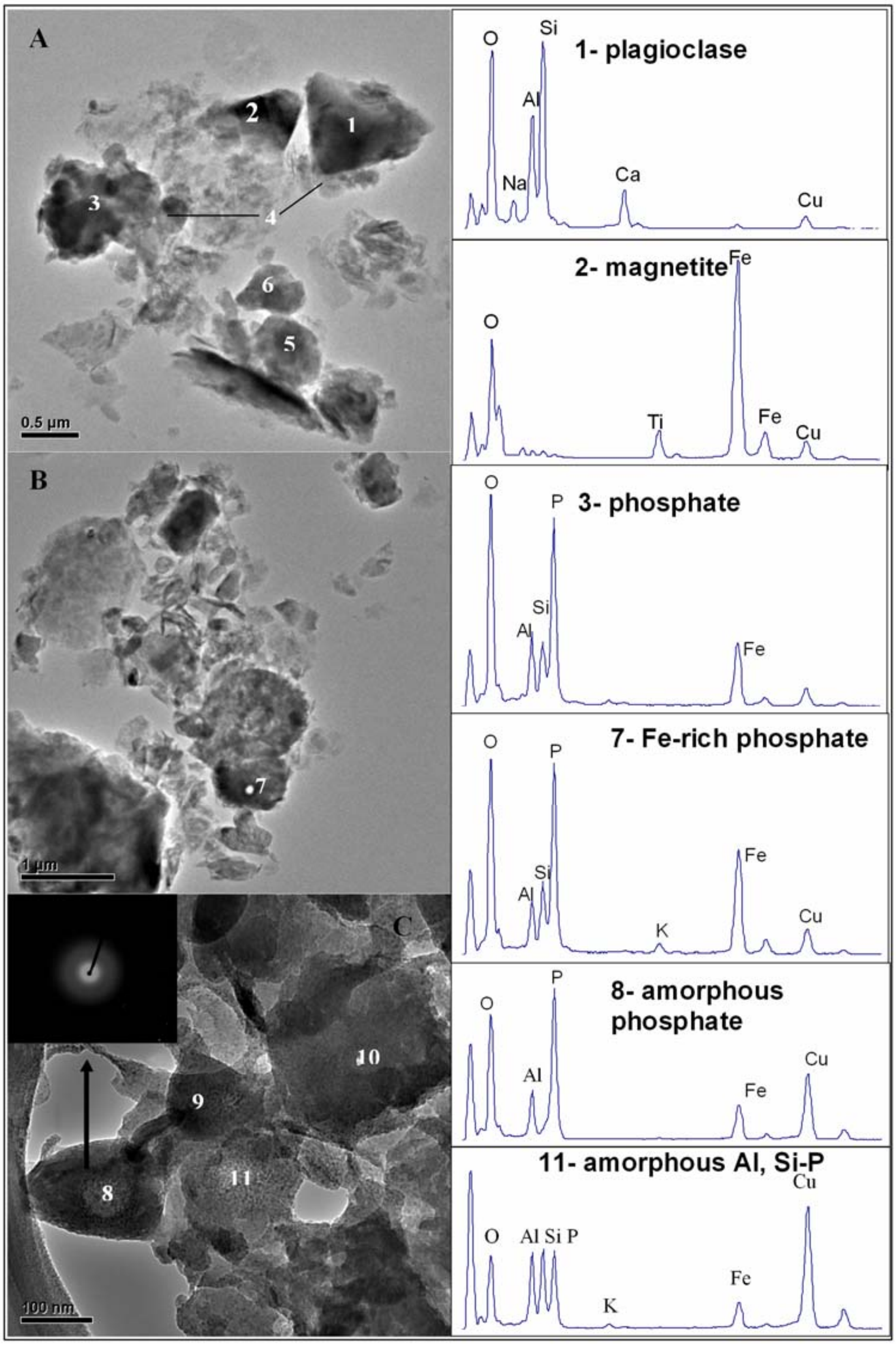

Figure 5 – TEM images, qualitative EDS analysis and electron diffraction of the clay fraction from Site 3. A) 1- plagioclase fragment; 2- Ti-rich magnetite; 3, 4 and 5- Al-Fe phosphates; 6- pyroxene. B) Fe phosphate in clay from site 3 after the sequential extractions (Fe-P). C) 7,8 and 9 – amorphous Al and Fe phosphates; 10- amorphous Al, Si and P phase. All features from C yielded electron diffraction patterns typical of amorphous materials (broad rings) as illustrated for C-8. Cu peaks in the EDS spectra are due to the copper grid.

The sequential extractions removed, on average, 53.5 (± 4.9) % and 72.3 (± 13.8) % of the clay fraction for Sites 3 and 4, respectively (Table 3-TMR). Similarly to Group 1, the amount of non-crystalline phases (organic matter bound and amorphous Al, Fe, Si-P minerals) was estimated from the mass removed by the pyr and ox extractions (Table 3).

The DXRD (pyr-ox) patterns of Group 2 clays present broad lines with maxima at 3.3 and 2.2 Å indicating the removal of amorphous minerals. The NaOH extraction resulted in the complete dissolution of crystalline phosphates for all samples from Site 4 (Figure 6) and for the deepest layer of Site 3 (not shown). For the upper layers of site 3, a crystalline phosphate with similar *d* values to leucophosphite persisted after the NaOH extraction (Figure 7). For samples from which all crystalline phosphates were dissolved, the mass removal by the NaOH extraction gives an estimate of the amount of these minerals (Table 3 – Site 3 and deepest layer of Site 4).

For Site 3, 41.4 (± 3.9) % of the clay fraction was removed by the *pyr* + *ox* extractions (non-crystalline phases). For Site 4 these phases account for 45.2 (± 9.4) % of the clay fraction. Approximately 73.2 % (Site 3) and 55.6 % (Site 4) of the non-crystalline components were removed by the pyrophosphate extraction evidencing the high participation of organic matter bound phases (Table 3). This was expected due to the high organic C content in these sites compared to Groups 1 and 3. At the deepest layer of Site 3, 24.7 % of the clay fraction was removed by the NaOH extraction (crystalline phosphates) and for Site 4, an average of 31.1 (± 5.3) % of the clay below 20 cm deep is composed of these minerals (Table 3).

For Sites 3 and 4 (Table 3), the oxalate extracts had the highest P levels of all sites (Site 2 - 72.0 ± 3.8 g/kg and Site 3 - 32.4 ± 3.0 g/kg) with the $P_2O_5/(Al_2O_3 + Fe_2O_3)$ ratio ranging from 0.7-1.0 and with extremely high values of the Al/Si ratio (Table 4). This suggests that amorphous Al and Fe phosphates were the main extracted phases. TEM/EDS analysis confirmed the abundance of spherical phosphate aggregates containing various amounts of Al, Fe and K (Figure 7). For the 20-40 cm layer of Site 3, P and Fe levels in the oxalate extracts were higher than for any of the other studied sites, with Fe exceeding Al (Table 3). On the other hand, for all layers of Site 4, Al levels are nearly two times higher than Fe in the oxalate extract (Table 3).

As described in detail by Polish researchers, various processes are responsible for the paragenesis of phosphates in ornithigenic soils of Maritime Antarctica (Tatur and Myrcha, 1993; Myrcha *et al*., 1985; Tatur and Barckzuc, 1985). Continuous manuring and high liquid water availability promote percolation of alkaline solutions which lead to the formation and persistence of phosphates. After site abandonment by penguins, soil acidification and percolation of alkali-poor rain or melt water cause the alteration and dissolution of these minerals, leading to the formation of amorphous Fe, Al-P phases.

Sites 3 and 4 are abandoned rookeries where exuberant vegetation has developed (Tatur *et al*., 1997; Chapter 2). Struvite and hydroxyapatite, typical of surface guano layers in active rookeries (Tatur and Myrcha, 1993), are no longer present due to their lack of stability in the current pedoenvironmental conditions. Nevertheless, even after a long period of abandonment, Al and Fe phosphates constitute the main crystalline components of the clay fraction for these sites thus constituting a long term reserve of P for plant nutrition. Previous works suggest that some of these rookeries are older than 500 years (Tatur *et al*., 1997).

The higher Fe levels in the oxalate extracts (Table 3) and the XRD patterns (Figure 6) suggest that the crystalline P mineral in the clay from the 20-40 cm layers of Site 4 is Fe-rich leucophosphite. TEM/ EDS analyses revealed the presence of Fe-rich phosphates in a sample from Site 4 previously extracted with NaOH, supporting this interpretation (Figure 7). This might explain the ineffectiveness of the NaOH extractant in removing the crystalline phosphates from these layers. Due to the insolubility of Fe at high pH (Smith, 1994), the NaOH extraction is not efficient in removing crystalline Fe-P minerals (Table 3, Figure 7).

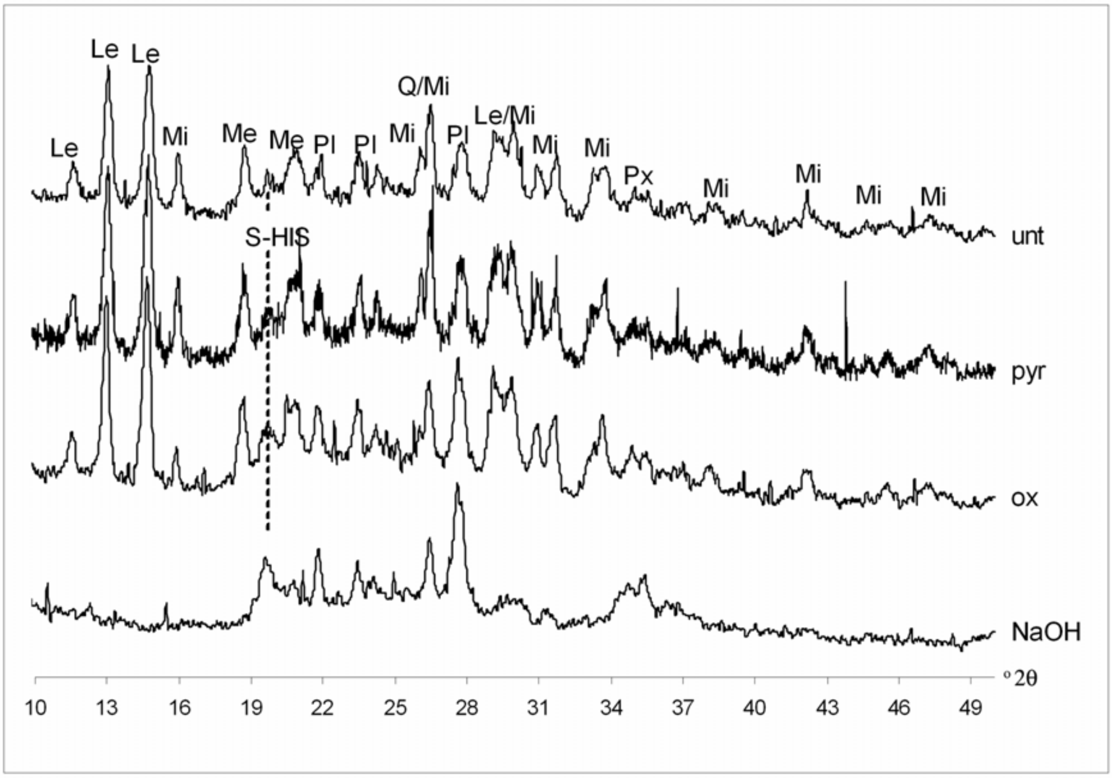

Figure 6 – Random powder XRDs of the clay fraction from a phosphatic layer of Site 4 after each chemical extraction. Le – leucophosphite; Me – metavariscite; Mi – minyulite; S-HIS - interstratified smectite-hydroxy-Al smectite; Pl-plagioclase; Q – quartz; Px – pyroxene; unt – untreated sample; pyr – after pyrophosphate extraction; ox – after pyr + oxalate extraction; NaOH - after pyr + ox + NaOH extractions.

Samples from sites 5, 6 and 7 do not contain crystalline phosphates. The TMR by the sequential extraction for each site was 38.9 (± 2.4) %, 57.4 (± 7.9) % and 54.1 (± 8.0) %, respectively (Table 3). Since for these sites little hydroxy-Al interlayer component and no crystalline minerals were removed, the TMR values give an idea of the amount of non-crystalline phases in the clay fraction from these sites. Similarly to sites 3 and 4, pyrophosphate-extractable phases account for approximately 60 % of the TMR, with increasing levels of Al, Si and Fe with depth (Table 3). For Site 6, a buried O horizon (30-

40 cm layer) favours the accumulation of Al and Fe bound to organic matter. The oxalate extract had a mean Al/Si ratio of 2.0 and relatively low P levels (7.8 – 15 g/kg), with the $P_2O_5/(Al_2O_3 + Fe_2O_3)$ ratios ranging from 0.3-0.6 (Table 4). NaOH extracted very little P and theAl/Si ratio < 0.9 of this extractant indicates the removal of an amorphous Si-rich phase(s) (Table 3).

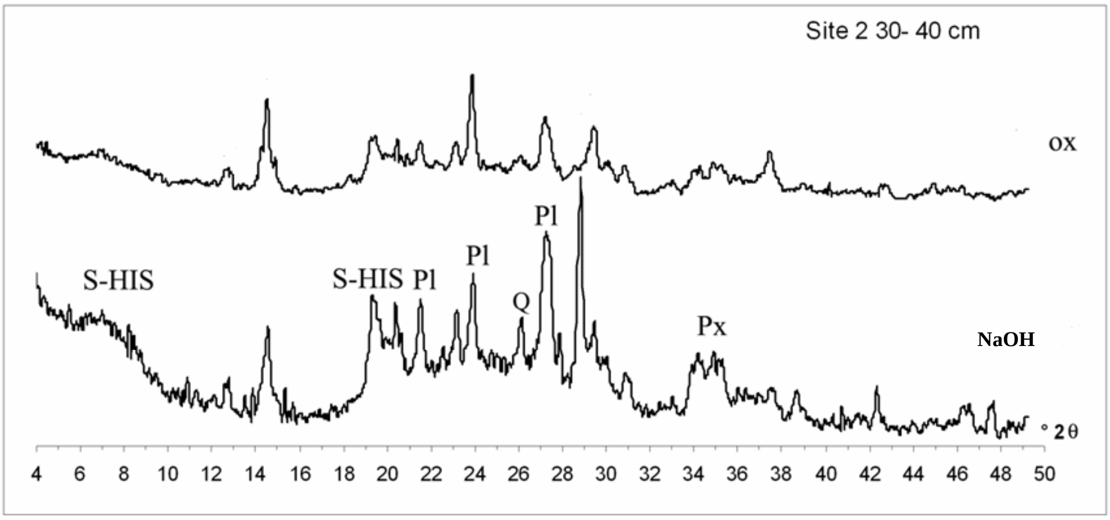

Figure 7 – Random powder XRDs of the clay fraction from Site 3 after oxalate (ox) and oxalate + NaOH (NaOH) extractions. An unidentified crystalline phosphate (P) yielding peaks similar to leucophosphite persisted after the NaOH extraction for the 30-40 cm layer while for the deepest layer (40 -50 cm) there was total removal of crystalline phosphates (not shown). S-HIS- hydroxy-interlayered smectite; Pl- plagioclase; Q- quartz; Px- pyroxene.

The composition of the oxalate extracts suggests that much P is adsorbed onto allophane-like phases for sites 5, 6 and 7. Due to the high organic C content (Table 2), some of the P is also likely to be adsorbed by humus-Al complexes. Allophane-like minerals, ferrihydrite and Al-humus complexes are the most likely to react with P in acid soils (Parfitt and Kimble, 1989). P-allophane reactions start with rapid strong adsorption followed by a slower, weaker adsorption. As the P concentration increases the disruption of the allophane structure, precipitation of crystalline or/and non-crystalline Al phosphates occurs. Even in soils where allophane is not present, aluminium phosphates can precipitate from reactions with Al-humus species if high levels of phosphate are present (Parfitt and Kimble, 1989). Similarly, reactions with amorphous iron oxides can lead to the formation of iron phosphates in acid (pH 2.3-4.9) pedoenvironments.

Amorphous Si-rich particles resembling grass opal phytoliths (Drees *et al*., 1989) are also common in the clay fraction for all ornithogenic sites but were not present in Groups 1 and 3 soils (Figure 8). This is consistent with the development of exuberant *Deschampsia Antarctica* (gramineae) communities at ornithogenic sites.

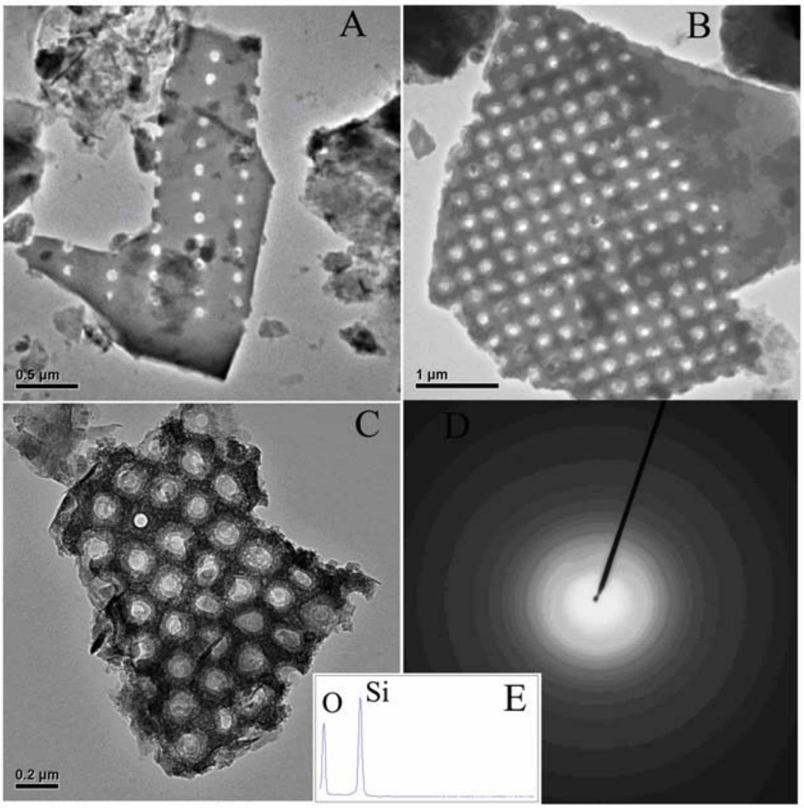

Figure 8 – Amorphous Si bodies (A, B, and C) in the clay fraction of ornithogenic soils, resembling grass root opal (Drees et al., 1989). All particles showed similar Si, O chemical composition (E) and electron diffraction patterns of amorphous silica (D), which are presented for feature A.

3.3 Group 3 - Acid sulphate soils (Sites 8 and 9)

Quartz and plagioclase are the main minerals in the sand fraction of these soils. Chlorite is also present with an intense peak at 7.06 Å and a much weaker peak at 14.2Å, corresponding to the 002 and 001 reflections. For the clay fraction, peaks at 24.4 Å, 12.07 Å and 8.1 Å after Mg saturation correspond respectively to the 001, 002 and 003 reflections of a regularly interstratified clay mineral composed of 10 Å and 14 Å layers (Figure 3). After glycerol solvation the 001 peak expanded to 27.6, with higher order reflections at 13.8 (002) and 9.4 Å (003), suggesting the presence of smectite layers (not shown). After K saturation, a peak at 21.5 Å was formed and heating to 550 ^{o}C yielded a 21.0 Å peak. These results suggest that the mineral is a regularly interstratified illite-smectite (I-S). Chlorite is also present in the clay fraction as evidenced by the 14.8 Å (001), 7.12 Å (002), 4.99 Å (003) and 3.54 Å (004) peaks, all unaffected by glycerol or K saturation. A peak at 1.50 Å (060 reflection) and no peak at 1.54 Å suggest a dioctahedral structure for the illite-smectite and possibly the chlorite (not shown) (Egli *et al*., 2001).

The XRD patterns of oxalate-extracted samples have peaks at 3.57 Å (kaolinite 002 peak) and 3.54 Å (chlorite 004 peak) (Figure 9A). After the urea treatment part of the 7.12 Å peak shifted to 7.6-7.8 Å, indicating the increase of kaolinite d_{001} values due to the penetration of urea into interlamenar spaces of kaolin (Gardolinki *et al*., 2001) (Figure 9B). The remaining 7.12 Å peak indicates the presence of chlorite, which was unaffected by the urea treatment. Results from DTA analysis (not shown) also support the presence of kaolinite with the main endothermic peak occurring between 460 – 490 ^{o}C while an incipient exothermic peak occurred between 950 – 1000 ^{o}C. Chlorite endothermic (600 ^{o}C) and exothermic (850 – 900 ^{o}C) peaks are also present. Based on TG data, the estimated total amounts of kaolinite in the clay fraction were 22.2 (± 0.3) % and 40.1 (± 2.8) % for Sites 8 and 9 respectively. TEM/EDS analyses confirmed the presence of kaolinite and indicate that it occurs mainly as rather asymmetrical plates and very rarely as typical hexagonal crystals (Figure 10 A and C). The electron diffraction patterns of the kaolinite crystals consist of a hexagonal *hk* network based on b = 9.0 Å.

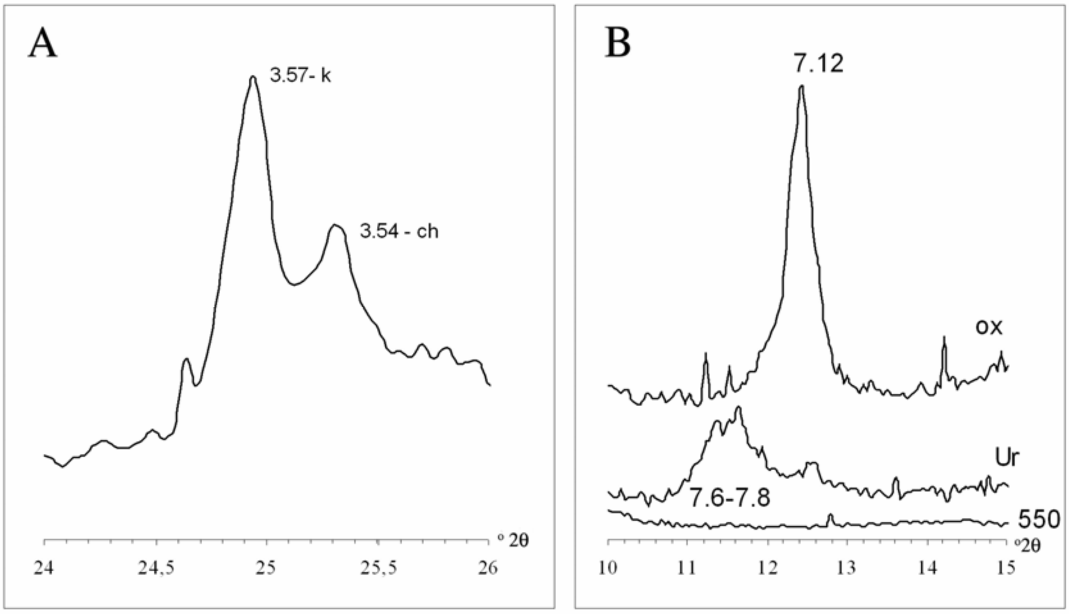

Figure 9 – XRD patterns of the clay fraction from Site 9 after pyrophosphate and oxalate extractions indicating the presence of both chlorite and kaolinite; Figure 9A shows distinguishable peaks at 3.57 Å for kaolinite and 3.54 Å for chlorite. Figure 9B shows the expansion of the kaolinite 001 peak to 7.6 – 7.8 Å after urea treatment, with no effect on the chlorite 002 peak.

The plagioclase content in the clay fraction is negligible with no characteristic sharp peaks at 3.19 and 3.20 Å. Jarosite was identified by the 5.09 (012), 3.08 (113) and 3.11 Å (021) reflections for Site 9 (Figure 11), although they were absent for Site 8. TEM/EDS analyses confirm the abundance of jarosite crystals in clay fraction of Site 9 (Figure 10 B). Various amounts of K and Na in the different jarosite crystals indicate that jarosite is commonly intermediate to natrojarosite .

Interstratified I-S, chlorite and kaolinite have been previously described for soils on King George Island and were attributed to paleohydrothemal alteration of mica-bearing granodiorites (Yong *et al.*, 2004). Wilson (1999) considers it unlikely that I-S form as a stable phase in soils due to the elevated temperature and pressures needed for its formation in diagenetic sequences. However, Bergkraut *et al*. (1994) have described regularly interstratified I-S formed under earth surface conditions due to weathering of basic pyroclastics. Środoń and Eberl (1984) also present evidences of illitization under pedogenic temperatures due to wetting and drying of smectites in the presence of K.

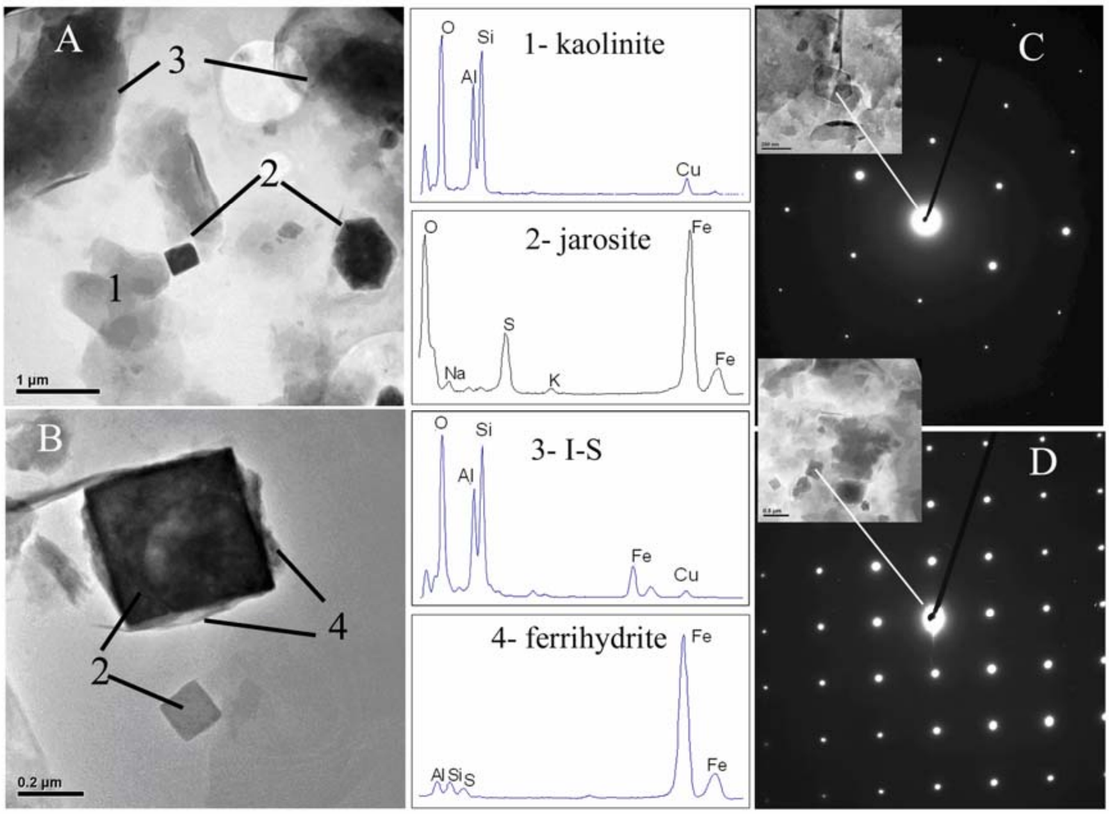

Figure 10 – TEM images and EDS of clay from Site 9. A) 1 – subheudral kaolinite plates; 2 –Jarosite crystals; 3 Interstratified illite-smectite; B) 4- ferrihydrite; C) electron diffraction pattern (EDP) of hexagonal kaolinite crystal and D) EDP of a single jarosite crystal.

Wetting and drying cycles take place in cryosols from Maritime Antarctica due to their frequent daily freeze-thaw cycles. Ultradessication of soils constituents due to freezing is an important, well-known process in cryosols (Ostroumov, 2004; Van Vliet-Lanoe *et al*., 2004). Under such conditions, illitization of smectites may take place. Sea-spray, bird droppings, weathering of plagioclases and transformation of jarosite to amorphous iron oxides are possible sources of K.

Oxidation of pyrite has resulted in acid sulphate weathering, with precipitation of jarosite and/or natrojarosite. As outlined by Doner and Lynn (1989), the acidity produced by this transformation has a strong impact on layer silicate stability, particularly for the interlayers of 2:1 silicates, leading to the degradation of chlorites and smectites. The absence of plagioclases in the clay fraction of Sites 8 and 9 suggests that chemical weathering is an important process at these sites. Although kaolinite may be inherited from the hydrothermal alteration of parent materials, chemical weathering of plagioclases to clay minerals is also a possible explanation for its presence in acid sulphate soils of Admiralty Bay.

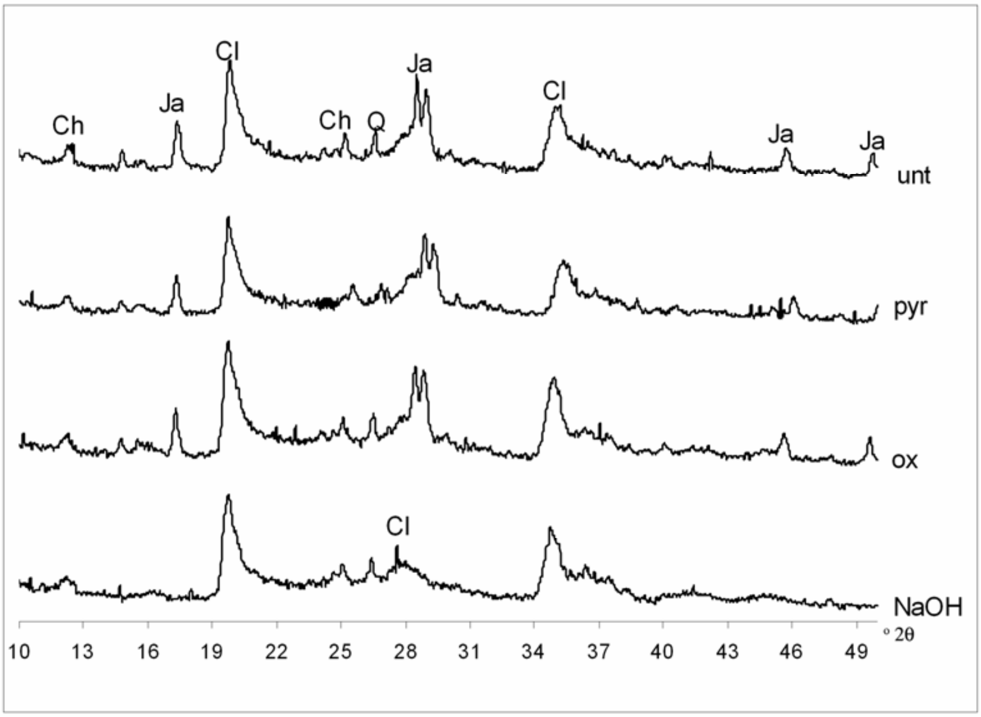

Figure 11 - Random powder XRDs of the clay fraction from Site 9, after each chemical extraction. (Cl – reflections common to all clay minerals, in this case chlorite, I-S and kaolinite; Ja – jarosite; Q – quartz; Ch - chlorite).

The TMR by the sequential extractions were 22.0 (± 1.0) % and 23.5 (± 2.9) % for Sites 8 and 9, respectively. Based on the mass removal by the pyrophosphate and oxalate extractions, non-crystalline phases account for 19.3 (± 0.4) and 14 (± 3.0) % of the clay fraction for Sites 8 and 9, respectively (Table 3). Pyrophosphate accounted for more than 60 % of the total mass removal for Site 8, while for Site 9 a gradual increase from 10 % to 40 % occurred with depth (Table 3). For both sites, pyrophosphate-extractable Al, Fe and Si increased with depth with an abrupt increase in the 20-40 cm layers of Site 9 (Table 3). Since these soils have negligible organic C contents, amorphous Al, Fe and Si compounds were probably the main phases extracted with pyrophosphate.

The oxalate extraction accounted for over 20 % of the TMR in Site 8. For Site 9, a gradual reduction from 40 % to 20 % with depth was observed (Table 3). The Fe levels for the oxalate extracts were very high (2-5 times higher than Al), suggesting that amorphous Fe (ferrihydrite) was the main extracted phase (Table 3). Relatively high P levels (comparable to some ornithogenic sites) suggest that is P adsorbed onto amorphous Fe minerals (Table 3). Weathering of mafic minerals such as pyroxenes and amphiboles, Fe-chlorite and hydrolization of jarosites are possible sources of amorphous Fe phases. A close association between amorphous Fe-rich phases and jarosite crystals was indicated by TEM/EDS analyses (Figure 10).

Boiling NaOH removed less than 20 % of the TMR for Site 8 and nearly 50 % for the first 20 cm of Site 9, with the amount gradually decreasing with depth to 35 % (Table 3). Jarosite was the main mineral removed by NaOH for Site 9 (Figure 11), with no effect of extraction on crystalline clay minerals. Therefore we can estimate that jarosite accounts for approximately 8-10 % of the clay fraction for this site.

These data suggest that intense acid weathering is occurring with accumulation of amorphous phases at depth. This is more noticeable for Site 9, where higher pyrophosphate-extractable Al, Si and Fe in the 20-40 cm layers (Table 3) coincide with the mean permafrost depth at this site. Accumulation of amorphous Fe, Al and Si gels in the permafrost table is common in cryosols, being facilitated by the thermally induced water potential starting from the onset of thaw (Van Vliet-Lanoe *et al.*, 2004).

4. Conclusions

Clay sized minerals on ahumic basaltic sites of Admiralty Bay are mainly inherited from hydrothermally altered parent materials through physical particle-size reduction promoted by soil freeze-and-thaw cycles. In the soil environment, these materials undergo chemical weathering with formation of interestratified S-HIS and allophane-like phases.

The interaction between penguin guano and inherited clay-sized minerals leads to the formation of crystalline Al and Fe phosphates which constitute long term P reserves on abandoned rookery sites on basaltic substrates. Leaching of P-rich solutions affects areas adjacent to penguin rookeries reacting with soil organic matter and allophane-like phases. The extremely high proportions of non-crystalline phases indicate the chemical characteristics of ornithogenic sites are determined by these highly reactive phases. Future monitoring of the chemistry of such phases may be useful in assessing anthropogenic impacts and environmental health.

Soils formed from sulphide-bearing andesites undergo intense acid sulphate weathering with formation of jarosite and amorphous Al-Si and Fe minerals. The clay fraction is constituted mainly of inherited interstratified I-S and chlorite as well as kaolinite. Intense weathering of primary plagioclases in these soils may lead to the formation of kaolinite.

Contrary to Antarctic continental cryosols, where physical weathering dominates, chemical weathering is an active process in cryosols from Admiralty Bay with dissolution of primary alumino-silicates and limited leaching of dissolved Al, Fe and Si. Chemical weathering is enhanced at some sites by the oxidation of sulphides present in the parent material and by faunal activity.

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CAPÍTULO 4

Micromorphology and microchemistry of Cryosols from Maritime Antarctica

1. Introduction

Micromorphological studies of permafrost-affected soils were pioneered by Fitzpatrick (1956), followed by the works Fedorova and Yarilova (1972), Fitzpatrick (1976), van Vliet-Lanoe (1976, 1982), Romans et al. (1980), Fox and Protz (1981), White and Fox (1997) and van Vliet-Lanoe et al., (2004). Fox and Protz (1981) showed that many different patterns of soils morphology result from cryogenic processes in Cryosols. A granular microstructure comprised of granic/granoidic fabrics is commonly observed in surface horizons, being replaced by a coalesced microstructure at depth (Smith et al., 1991; Tarnocai et al., 1993; White and Fox, 1997). Platy structure having a banded fabric has been reported to occur in Cryosols subjected to freezing and thawing processes (van Vliet-Lanoe, 1985; Gubin, 1994). Experimental work on freeze-and-thawing in frost-susceptible soils demonstrated the development of fragmic and microbanded micromorphologies (White and Fox, 1997).

Several studies indicate that soils from Maritime Antarctica are more developed than that from dryer and colder climatic zones of Antarctica (Blume et al., 2004; Michel et al., 2006). We studied in detail the soils from Admiralty Bay, King George Island and identified four main soil groups (Chapter 1), as follows: i) basaltic/andesitic soils; ii) acid sulphate soils; iii) soils under weak ornithogenic influence; iv) ornithogenic soils.

Although physical weathering is without doubts a major soil forming process, chemical weathering also occurs especially in acid sulphate and ornithogenic soils (Chapter 3). The latter are strongly affected by sea-land transfers of nutrients by sea birds, mostly penguins, through deposition of large amounts of guano during the Antarctic summer. In these soils, a particular and complex process of deep soil phosphatization occurs, as described in some detail by Tatur & Barczvk (1985) and Tatur (1989), followed by Schaefer et al., (2004).

Micromorphological and microchemical studies reveal important information regarding soil genesis and physico-chemical behaviour. There are few such studies for soils from Antarctica (Fitzpatrick, 1956; Kubiena, 1970; Jeong and Yoon, 2001). In general, soils from cold regions are typically dominated by primary inheritance from the parent rock, subjected to intense cryoturbation processes (Van Vliet-Lanoe et al., 2004) and pedogenesis displaying features such as concentric deposition of clay particles on sand grains (Korina and Faustova, 1964). Therefore, microfabric development is greatly influenced by the characteristics of the lithological fabric. Different types of platy and granular fabrics (van Vliet-Lanoe, 1985) and elluviation-illuviation processes (Fox and Protz, 1981) are commonly reported for cryogenic soils.

The objective of this paper was to describe and analyze the most important micro and sub-micromorphological features of basaltic/andesitic, acid sulphate and ornithogenic Cryosols from Admiralty Bay, Maritime Antarctica.

2. Material and Methods

2.1 Study area

The Admiralty Bay (62°03’40”-62°05’40” S and 58°23’30”-58°24’30” W) is located in King George Island and is part of the South Shetlands Archipelago, Maritime Antartica (see map in Chapter 1). Data sets from 1982-2002, acquired at the Brazilian Comandante Ferraz Station, report mean air temperatures varying from -6.4 °C in July to + 2.3 °C in February. Mean annual precipitation is 366.7 mm. Positive air temperatures are observed from November until March when effective precipitation as liquid water is increased due to melting of accumulated winter snow.

2.2 Soils

We have selected four pedons for this study, representing the main soil types commonly found in ice-free areas of Admiralty Bay. Some characteristics of the studied soils are presented in Table 1. Detailed chemical, physical and mineralogical data regarding these soils are found in the previous Chapters of this thesis.

Table 1 – Some chemical, physical and mineralogical characteristics of the studied soils.

Pedon	Parent Material	Mineralogy/1	pH/2	P/3	Al/4	TOC/5	Texture
		clay fraction	H_2O	mg/dm^3	cmol$_c$/dm^3	g/kg	
A10 – Typic Haploturbel	Basaltic/andesitic till	HIS:S> fel, pyr	6.8 (±0.3)	56.6 (±11.9)	0.3 (±0.2)	1.0 (±0.2)	Sandy loam
K24 – Sulphuric Haploturbel	Sulphide bearing andesites	ka = ch > I:S > ja > fer	4.5 (±0.3)	21.3 (±4.0)	27.7 (±7.3)	1.2 (±0.4)	Silt loam
A3 – Ornithogenic Psammoturbel	Basalt/andesitic till and penguin guano	A.P. > le > va >HIS:S > feld, pyr	4.1 (±0.3)	1421.8 (±310.3)	6.2 (±1.5)	13.0 (±2.3)	Sand
A4- Ornithogenic Psammoturbel	Basalt/andesitic till and penguin guano	A.P. > le > va , mi >HIS:S > feld, pyr	4.2 (±0.1)	1015.3 (±267.4)	10.5 (±2.5)	6.0 (±2.7)	Sandy loam

/1 clay fraction mineralogy according to the data presented in Chapter 3 of this thesis, HIS:S – intestratified semectite: hydroxi-interlayered smecticte, fel- feldspar, pyr – pyroxene, ka – kaolinite, ch – chlorite, I:S – interstratified illite:smectite, ja – jarosite, fer – ferrihydrite, A.P. – amorphous phosophate, le- leucophosphite, va – variscite, mi- minyulite; /2 measured in 1:2.5 soil:water ratio; /3 extracted with Melich-1; /4 exchangeable Al extracted with 1 mol/L KCl; /5 total organic carbon measured by wet combustion (Yeomans and Bremner, 1988)

2.2 Micromorphology

Undisturbed soil blocks were sampled at different depths for each soil, dried at 50 ^{o}C and impregnated with a 1:1 crystic resin: stiren mix poured onto samples at atmospheric pressure. Impregnated samples were cut into slabs of 0.5 cm thickness using a diamond saw, and polished with corundum 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 nm thick sections. No cover slips were used. 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 pedogenic 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-EDS analysis.

Electron microscopy analysis: SEM/EDS

The microstructure and submicrostructure were investigated using a JEOL 6400 and a Zeiss scanning electron microscopes both coupled with an Oxford Instruments energy dispersive X-ray detector (SEM/EDS), following the recommendations of Bisdom and Ducloux (1983). Microchemical analyses were acquired at 17 to 18 mm working distance and 15 kv.

3. Results and discussion

Pedon A10 – Typic Haploturbel

The main micro and submicroscopical pedofeatures described for this pedon and their chemical composition are presented in Table 2.

This soil has a poorly sorted, clast-supported fabric for the upper 10 cm changing with depth to a moderately sorted, matrix-supported fabric. Lithic clasts of porphyritic lavas (andesitic to basaltic) occur in several size ranges (< 2 mm and > 2mm), evidencing that physical weathering and particle-size reduction through freeze-and-thawing is indeed a very efficient process in Maritime Antarctica.

Clasts are angular to sub-angular in the coarser size fractions (> 2 mm) and present increasing degree of rounding and sphericity with decreasing particle size (Figure 2).

Plagioclase is the main phenocryst mineral and varies from fresh and unaltered to strongly altered, corroded grains which are normally replaced by a brownish clay mineral (Figure 2) with high Mg level as indicated by the elemental maps and quantitative EDS analysis (Figure 3 and Table 2). Pyroxenes are also common phenocrysts (Figure 2, 3 and Table 2). Most of these porphyritic lavas have a very dark, opaque and isotropic, oxidized groundmass, with microcrystalline mafic minerals and plagioclase (Figures 2 and 3), while others present microcrystalline lighter coloured groundmass. Holocrystaline and glassy/microcrystalline clasts of non-porphyritic lavas as well as devitrified/altered glass of several colours and types are common. Lithic clasts vary widely in colour suggesting different degrees and types of oxidation and alteration. We did not observe evidences of ash-fall such as pumice shards like those reported by Jeong and Yoon (2001) for soils from nearby areas in King George Island.

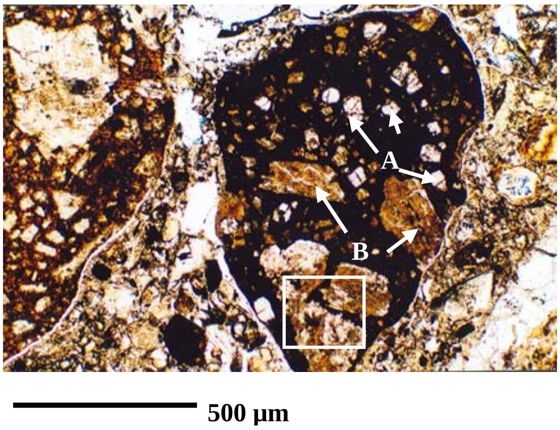

Figure 2 – Photomicrograph of pedon A10 showing two sub-angular, sand-sized clasts with opaque, isotropic mass and abundant phenocrysts of pyroxene (A) and plagioclase (B). The latter are strongly altered and replaced by a brown earthy mass . Smaller size-fractions have increasing roundness and show the same composition of larger clasts. The backscattered electron image and elemental maps for the area marked with the square are presented in Figure 3.

Individual, mostly single crystal mineral grains are common in the < 2 mm fractions. Plagioclase feldspars showing various degrees of alteration (Fitzpatrick, 1993) are the most common grains, but pyroxenes and magnetite are also common. Silty and clayey capping around primary mineral grains forms sub-rounded aggregates (Table 2). Illuvial deposition of clay on clast surfaces was also observed (Figure 4 and Table 2).

Table 2 – EDS analysis of micropedological features observed in Pedon A10 and illustrated in Figures 2, 3 and 4. (n = number of analyses, n.d. = not detected).

Pedofeature	**n**	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**K_2O**	**CaO**	**TiO_2**	**FeO**	**Total**
							%			
					Clasts					
A[1] – Pyroxene	3	0.5 ± 0.1	16.3 ± 0.3	1.9 ± 0.1	52.3 ± 0.1	n.d	17.7 ± 0.2	0.6 ± 0.1	11.7 ± 0.4	101.7 ± 0.3
B[1] - Plagioclase-Na	7	10.3 ± 0.2	n.d	21.3 ± 0.3	70.0 ± 0.8	n.d	1.2 ± 0.3	n.d	0.1 ± 0.1	102.8 ± 1.0
C[2] - Clay mineral replacing plagioclase	10	0.7 ± 0.7	8.2 ± 1.2	25.5 ± 2.5	39.9 ± 3.2	1.3 ± 0.3	1.0 ± 0.1	n.d	4.4± 0.9	81.4 ± 4.5
					Silte sized aggregates					
Plagioclase-Ca	7	1.4 ± 2.3	0.2 ± 0.3	20.7 ± 3.0	52.7± 3.3	0.5 ± 0.3	9.8 ± 2.4	n.d	0.5 ± 0.4	85.9 ± 4.2
Ti-silicate	1	2.4	0.3	9.7	42.1	0.4	20.6	19.4	3.01	98.2
Matrix	6	0.5 ± 1.0	5.3 ± 2.0	24.3 ± 6.0	45.6 ± 4.9	0.7 ± 0.4	3.9 ± 4.0	n.d	4.1 ± 2.0	84.5 ± 5.7
Matrix	4	0.1± 0.1	20.4 ± 3.0	10.2 ± 1.6	45.0 ± 4.4	0.1 ± 0.2	1.6 ± 0.7	n.d	7.5 ± 5.2	84.9 ± 6.0
D[3] - Illuvial feature	3	0.1 ± 0.1	18.6 ± 0.6	12.33 ± 0.6	37.27 ± 0.6	n.d	1.6 ±0.1	n.d	6.6 ± 0.2	76.7± 0.9

[1] illustrated in Figures 2 and 3; [2] illustrated in Figure 3; [3] illustrated in Figure 4

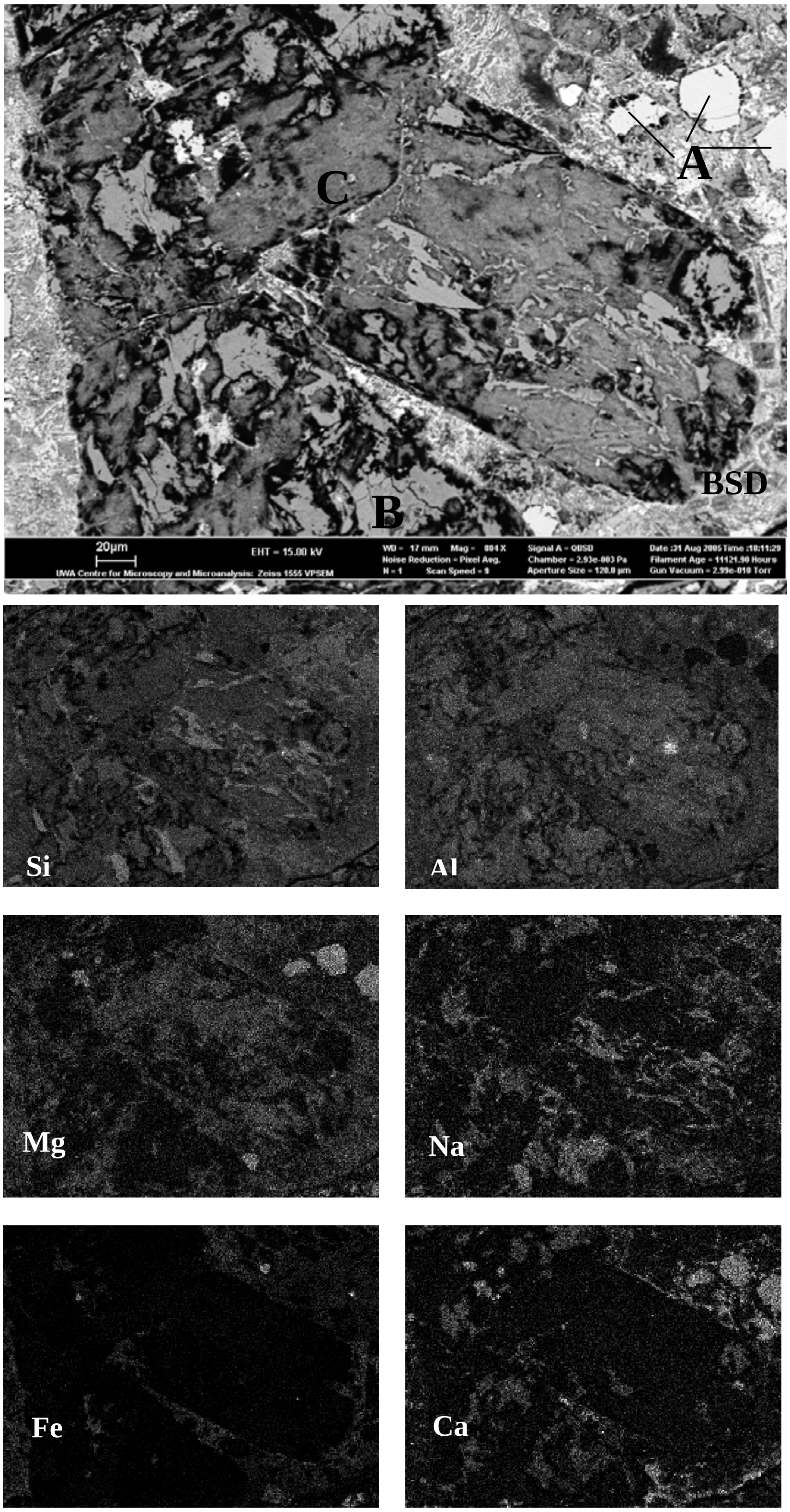

Figure 3 – Backscattered electron image (BSD) and elemental maps (Si, Al, Mg, Na, Fe and Ca) of the area indicated by the white box in Figure 2. A – pyroxene crystals in a microcrystalline matrix composed of mafic minerals and plagioclase; B - remainings of Na-plagioclase phenocryst; C-. clay mineral replacing plagioclase

The highly diverse composition of clasts and grains indicate that this soil is formed from the extensive mechanical reworking of a variety of source rocks. This was expected as a result of soilfluxion, cryoturbation and other periglacial processes. We could not distinguish any zonation in the alteration of large clasts and mineral grains, which suggests little chemical weathering. The chemical analyses show that the fine particles and silt-sized aggregates have MgO levels varying from 5.3 to 20.4 % (Table 2) suggesting that smectites and/or chlorites are the main clay minerals. Jeong and Yoon (20001), reported that smectites formed from volcanic glass in Barton Peninsula had significantly higher levels of MgO (6.27 ± 1.28 %) and Fe_2O_3 (17.76 ± 1.2 %) than that formed directly from the bedrock (2.76 and 2.21 % of MgO and $Fe_2O_{3,}$ respectively$_{)}$.

The data shown in Chapter 3 indicates smectite in the clay fraction of pedon A10 but not chlorite. Therefore, we postulate that chlorite is inherited, being formed during hydrothermal alteration of primary rock minerals and gradually altered to smectite in the soil environment through chemical weathering.

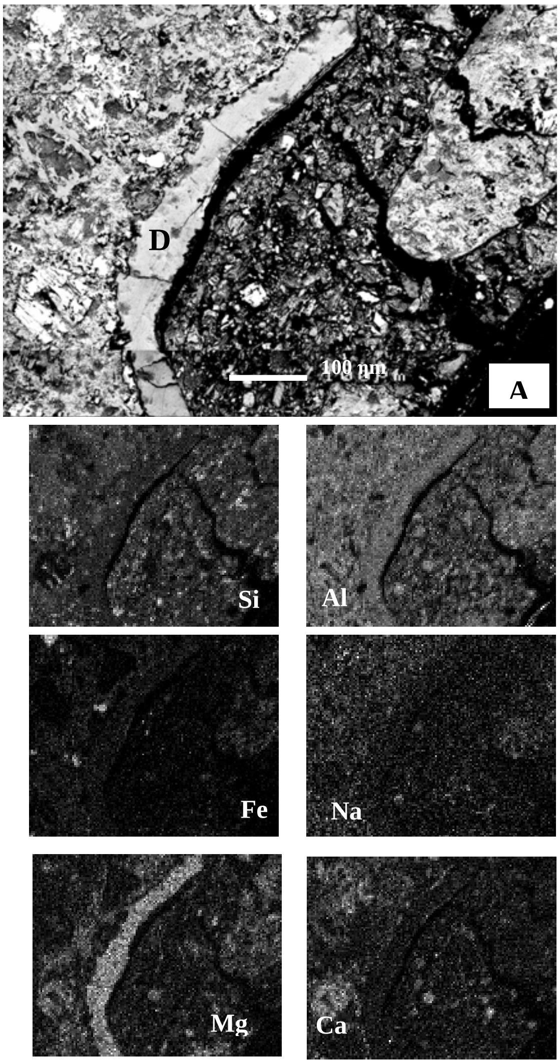

Figure 4 – BSD image and elemental maps (Si, Al, Fe, Na, Mg and Ca) for pedon A10 showing an illuvial clay deposit (D) with high Mg levels. The fine fraction is composed mostly of sub-rounded fragments of primary minerals.

Pedon K 24 – Sulphuric Haploturbel

The main micro and submicroscopical pedofeatures described for this pedon and their chemical composition are presented in Table 3 and illustrated in Figures 5, 6 , 7 and 8.

This soil presents isotropic yellowish matrix-supported fabric (Figure 5-A) exhibiting a well developed medium-sized granular structure (Figure 5-B), typical of some Cryosols (Van Vliet-Lanoe *et al*., 2004). The granular structure in Cryosols is well documented and is formed due to differential frost heave, rotation and ultradessication, resulting in highly stable sub-rounded peds (Van Vliet-Lanoe et al., 2004). The acidic nature of acid sulphate soils, with presence of kaolinite in the clay fraction favours flocculation of fine particles and chemical stabilization of microaggregates.

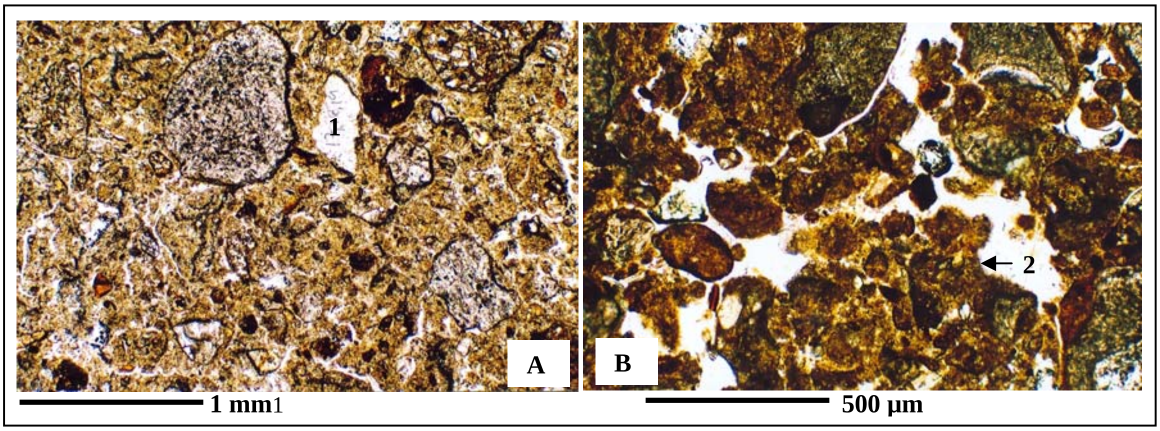

Figure 5 – Photomicrographs of pedon K24. A – Yellowish matrix-supported fabric with medium granular structure and deposits on the surfaces of coarser grains. Strongly altered andesitic clasts with abundant plagioclase phenocrysts show increasing degree of roundness with decreasing particle size. A large kaolinite fragment can be observed (1). B- Detail of the extremely well developed medium-sized granular structure (2). Aggregates normally contain high proportions of secondary silica and primary minerals.

The soil matrix is composed by a silty mass with Si-rich precipitates, Fe-Ti oxides and sulphides (pyrite) (Figure 6). The microanalysis of the fine fraction revealed variable levels of K and Fe (Table 3). In some cases the chemical composition is very similar to that commonly reported for kaolinte. In others, higher levels of Fe and K suggest interstratification of Fe-rich smectite and illite. The fine matrix is most likely a mixture of kaolinite and complex interstratified minerals. This is in agreement with Simas et al. (2006b) who reported the presence of such minerals in the clay fraction of this soil. Jeong and Yoon (2001) also reported the occurrence of an interstratified illite:smecite mineral with 4.9 % K_2O as well as kaolinite for soils from granodiorites in Barton Peninsula.

The elemental maps and microanalyses indicate that the oxidation of sulphides results in intense chemical weathering and Fe mobilization in pedon K24 with formation of jarosite and amorphous Fe minerals (Figure 7). These results are in agreement with the conclusions presented in Chapter 3, that soils formed from sulphide-bearing andesites undergo acid sulphate weathering with formation of jarosite and amorphous Al-Si and Fe minerals (ferrihydrite).

Most andesitic clasts are strongly altered and present embayment of alteration products and illuvial Fe-rich precipitates filling dessication fractures and hydrothermal veins. These features are bright red at OTM level (not shown) and produce intense backscattering in the SEM image (Figures 7 and 8). Coarse kaolin fragments were also present indicating intense weathering of primary alumino-silicates (Figure 5 and Table 3).

In Figure 8, it is observed the dissemination of jarosite (S associated with Fe and K) within a K-rich matrix of a volcanic clast. In the same figure, evidences of intense chemical weathering can be observed such as the secondary silica precipitates enclosing altered phenocrysts of Na plagioclase. During pedogenesis, the strong acidity released by the oxidation of pyrites attacks rock fragments. The hydrolysis of silicates produces monomeric silica which may precipitate or polymerize to form several minerals depending on the environmental conditions (Norton, 1994).

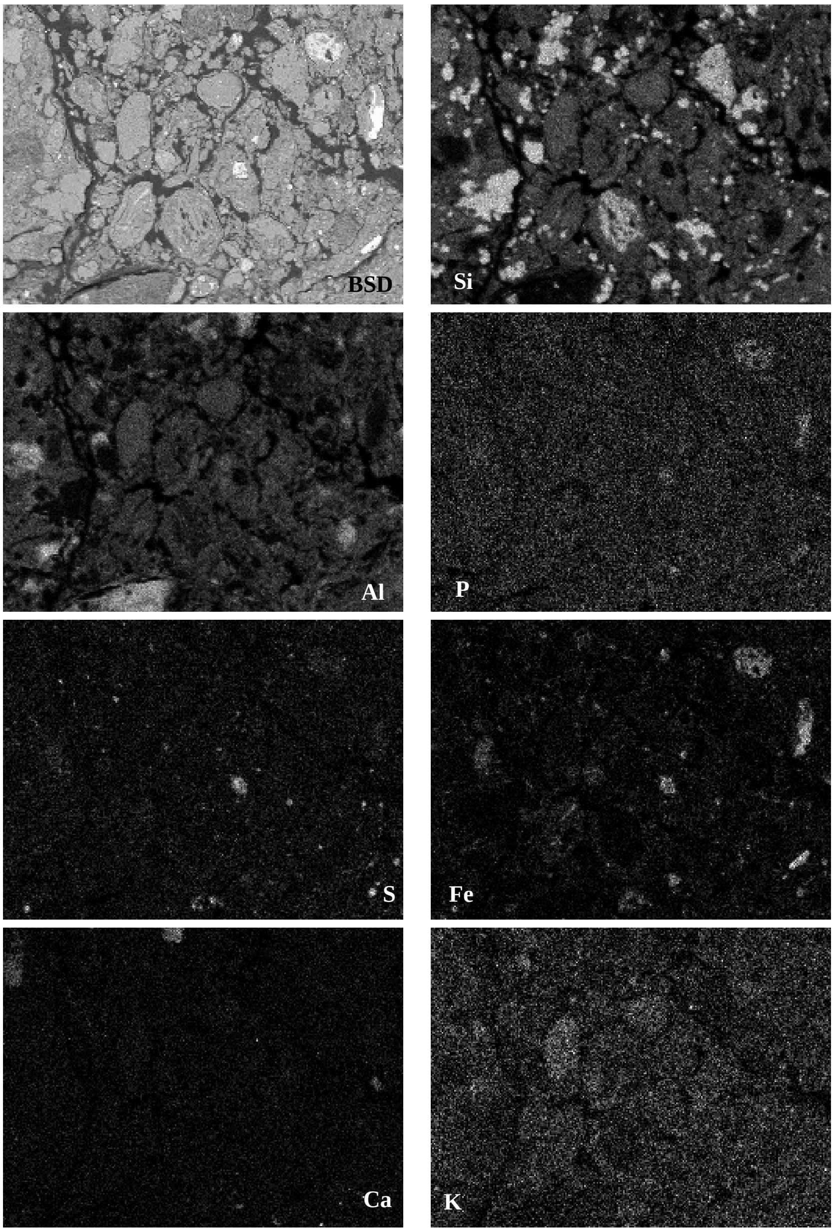

Figure 6 – BSD electron image and elemental maps (Si, Al, P, S, Fe, Ca and K) showing the well-developed granular structure in pedon K 24 composed of a silty matrix containing mainly Al, Si and K with secondary Si phases, iron oxides and S-rich minerals (sulphides and sulphates).

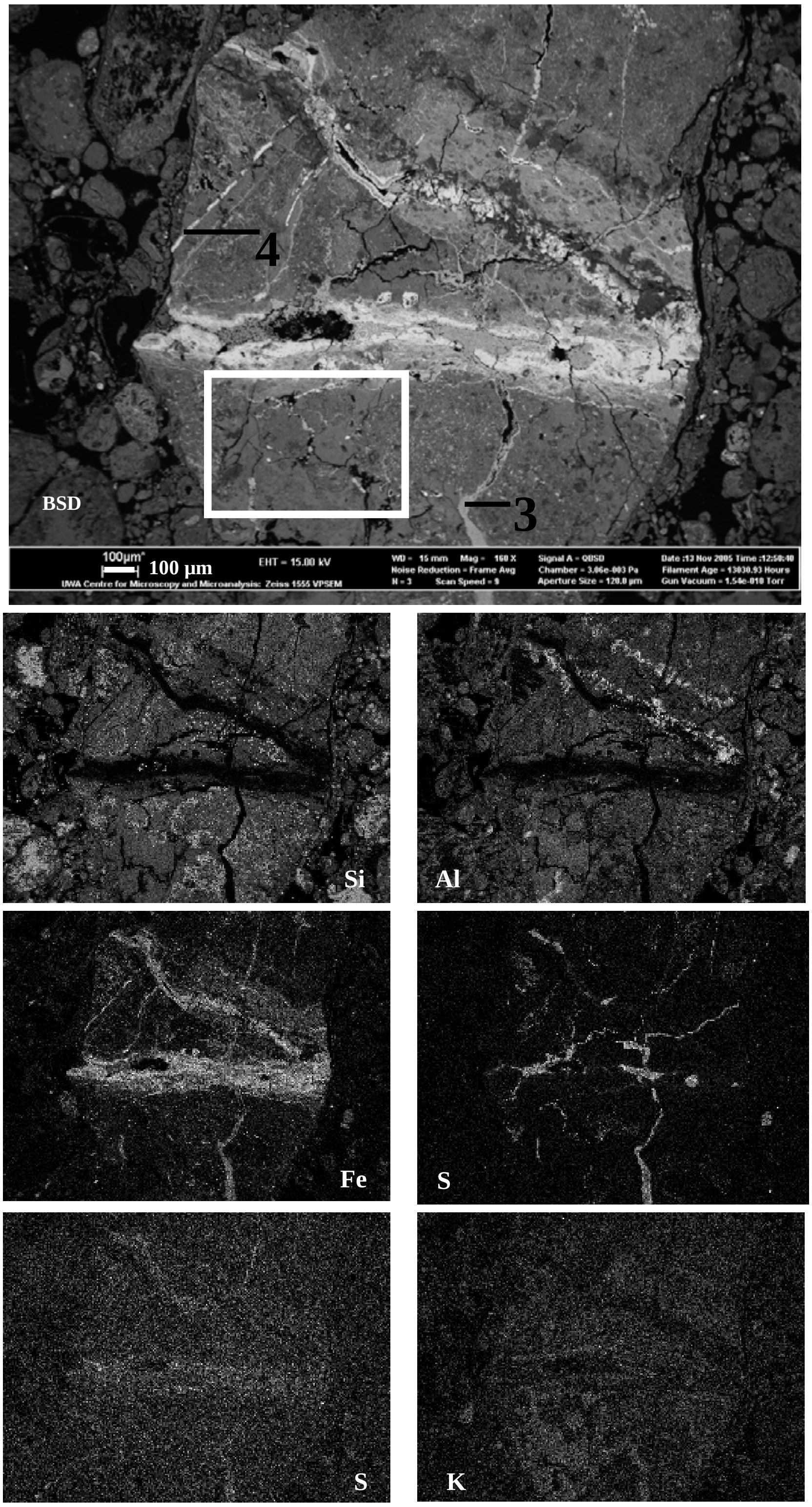

Figure 7 – BSD image and elemental maps (Si, Al, Fe, S and K) of altered andesitic clast with embayemt of Fe-rich phases (4). Jarosite is present along cracks and ped surfaces (3). A detailed study of the area indicated by the white square is presented in Figure 8.

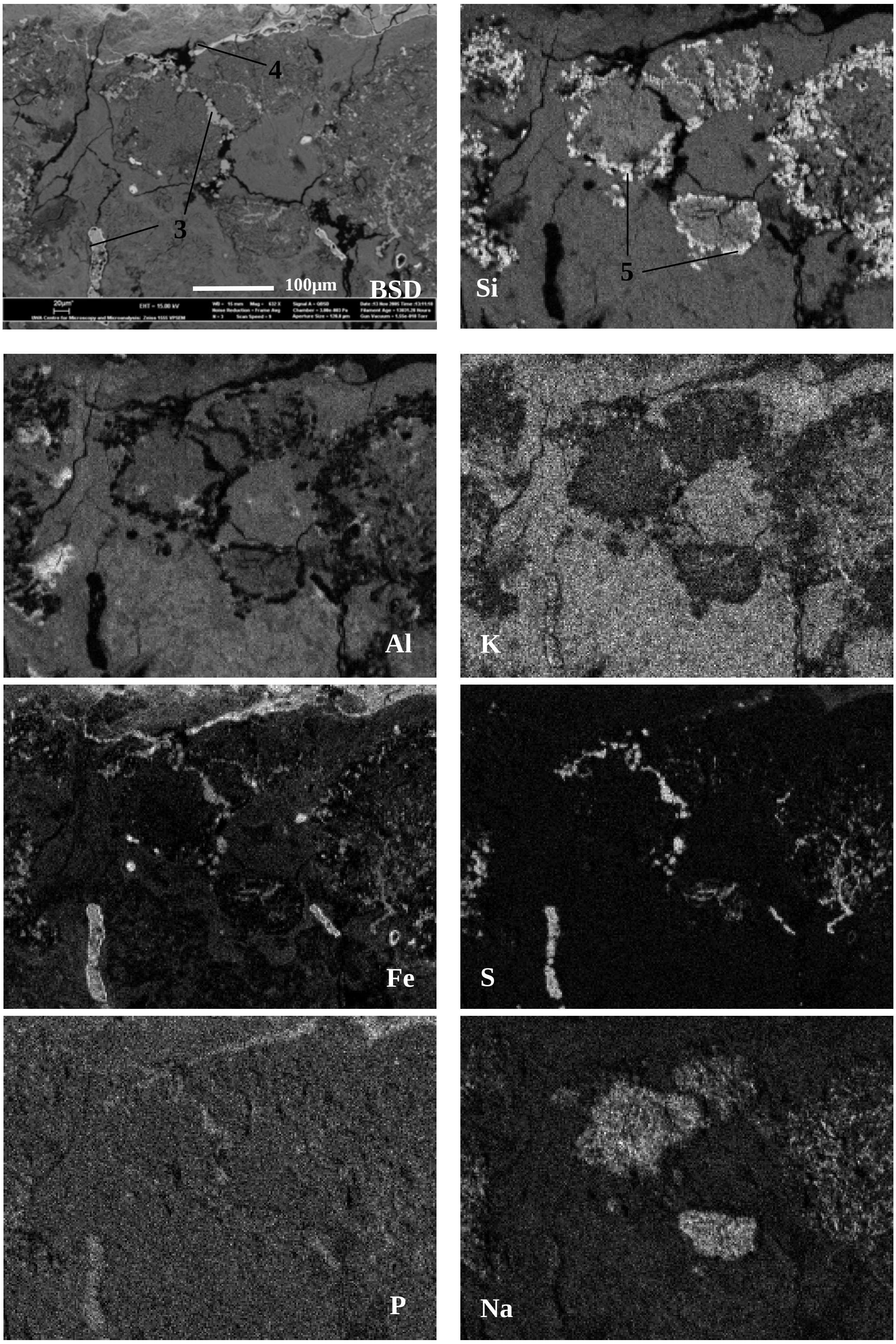

Figure 8 – BSD image and elemental maps (Si, Al, K, Fe, S, P and Na) of the area indicated in Figure 7. Jarosite (3) and Fe-rich phases (4) are present. Observe the formation of secondary Si phases (5) around Na-plagioclase crystals due to the acid attack of primary minerals promoted by sulphide oxidation.

Jarosite is metastable in soils and can hydrolyse to form goethite or amorphopus Fe depending on soils redox potential and pH (van Breemen and Harmsen, 1975; Donner and Lynn., 1989; Fanning and Rabenhorst, 1990). The elemental maps (Figures 7 and 8) illustrate the close affinity between P and the Fe-rich fillings in the studied soil suggesting that these are very reactive amorphous Fe phases with high P adsorption capacity. Point-source analyses reveal that ferrihydrite presented the highest P levels, followed by jarosite (Table 3). The low totals obtained for both minerals indicate that these are poorly crystalline, highly hydrated and beam-sensitive phases

Table 3 – Chemical composition of some important pedofeatures in acid sulphate soil from Admiralty Bay (pedon K24).

Pedofeature	**n**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**K_2O**	**Fe_2O_3**	**Total**
				%				
1[1] - soil matrix	30	29.0 ± 4.2	46.5 ± 6.8	0.1 ± 0.2	0.7 ± 1.0	1.5 ± 0.9	3.9 ± 3.3	89.8 ± 0.2
2[1] - kaolinite	3	35.0 ± 2.0	45.8 ± 3.0	n.d.	n.d	0.2 ± 0.1	n.d.	81.4 ± 2.5
Ref. kaolinite[/1]		39.5	46.6	-	-	-	-	86.1
3[2] - jarosite	8	1.6 ± 1.2	2.1 ± 1.7	1.6 ± 0.3	20.9 ± 3.8	2.72 ± 0.8	35.7 ± 2.2	66.4 ± 1.7
Ref. Jarosite[3]	-	-	-	-	31.9	9.4	47.8	89.2
4[2] - ferrihydrite	23	3.1 ± 1.6	3.42 ± 2.38	3.3 ± 1.5	5.4 ± 2.5	0.1 ± 0.3	53.4 ± 4.9	69.4 ± 3.7
Ref[3]. ferrihydrite[3]	-	-	-	-	-	-	94.6	94.6

[1] illustrated in Figure 5; [2] illustrated in Figures 7 and 8; [3] data obtained from www.webmineral.com; - not detected

Pedons A3 and A4

These pedons are located close to Rakusa Point and represent typical ornithogenic soils from the western shore of Admiralty bay. They have an accumulation of surface fibric organic matter formed by abundant talii of bryophytes and lichens, as well as grass roots, changing abruptly to a mineral phosphatic horizon of bleached colours, showing a medium-sized granular structure of sub-rounded forms, including varied pedogenized ornithogenic materials, such as P-rich organic remains, nodular phosphates forms (Figure 9) and fragments of bone apatite (Table 4). The granular aggregates are silty, with low clay content, and usually surrounded by secondary, illuvial pedogenic P deposition. The elemental mapping showed that the fine fraction is dominated by phosphatic aggregates (Figure 9).

At the OTM level, illuvial phosphatic features occur as bright yellow infillings along cleavage lines or broken, cryoturbic fragments of rocks and aggregates (Figure 10 feature A). The P-rich solution penetrates in the cracks and reacts preferably with highly reactive volcanic glass forming a framework of phosphatic rims around glassy materials.

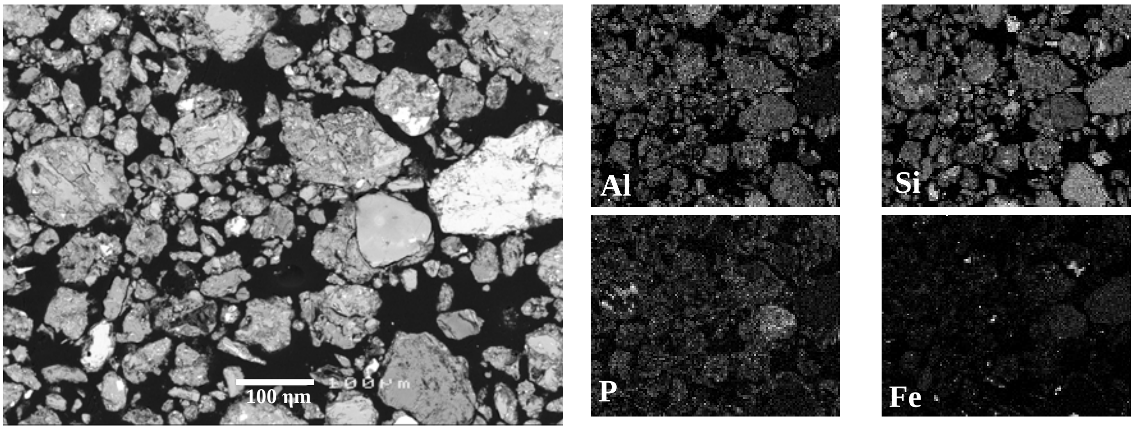

Figure 9 – BSD image and elemental maps (Al, Si, P and Fe) of pedon A3 showing the typical granic/granoic granular microstructure with high P content.

The mean composition for some typical phosphatic features is given in Table 4. Bone apatite is the most common primary phosphate in ornithogenic soils from abandoned penguin rookeries (Table 4-I). All secondary P forms are depleted in Ca, Mg and Na with variable levels of Al and Fe, and relatively low Si values.

The detailed analyses of the phosphatization of volcanic glass (Figure 10 and Table 4 - A, B and C) show a gradual increase of P levels from the inner to the outer part of the glassy feature accompanied by Si depletion and relative Al enrichment. This is similar to the results from Parfitt, (1989) studying the reaction of P-rich solutions with amorphous minerals. He reports that as P levels in the solution increased, the structure of allophane was gradually disrupted, with displacement of Si to the solution. As this reaction proceeds, crystalline and/or amorphous Al and Fe phosphates precipitate. Analogously, in ornithogenic soils, P-rich solutions react with volcanic glass and release Si to the solution while P is incorporated, resulting in the formation of secondary P minerals.

The phosphatization is not restricted to volcanic glass and is also common on other lithological features such as the microcrystalline matrix of clasts as illustrated in Figure 11. As expected, the chemical composition of the secondary phosphate reflects the nature of the lithofragment which is being phosphatized. Al phosphates with low Fe levels are usually related to Al/Si volcanic glass while Fe-rich phosphates are formed from the reaction with the mafic microcrystalline matrix of the basaltic/andesitic clast (Figure 11 -and Table 4).

Secondary crystalline Al and Fe phosphates were also analysed (Table 4 - G and H). These minerals had both the highest P_2O_5 (31.7 %) and the lowest SiO_2 (3.7 to 9.8 %) levels amongst all the analyzed features.

Table 4 – Chemical composition of phosphatized features in pedons A3 and A4, illustrated in Figures 11 and 12.

Pedofeature	**n**	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**K_2O**	**CaO**	**TiO_2**	**Fe_2O_3**	**Total**
A – outer margin of illuvial phosphatic coating	9	0.5 ± 0.0	2.6 ± 1.3	15.1 ± 0.6	21.9 ± 3.1	24.4 ± 4.5	1.5 ± 0.0	1.8 ± 1.3	1.7 ± 1.4	13.5 ± 0.4	82.9 ± 2.9
B – center of phosphatic coating	9	0.2 ± 0.1	0.8 ± 1.4	11.0 ± 0.7	43.1± 11.9	12.8 ± 3.4	0.9 ± 0.2	0.3 ± 0.1	0.3 ± 0.1	7.0 ± 3.6	76.5 ± 4.5
C - inner border of phosphatic coating (phosphatized glass)	6	n.d	n.d	8.0 ± 0.6	75.5 ± 3.1	3.6 ± 0.8	0.3 ± 0.0	0.1 ± 0.1	0.0 ± 0.0	n.d.	89.3 ± 6.8
D – phosphatized volcanic glass	3	0.2 ± 0.2	0.8 ± 0.6	9.0± 0.5	51.6 ± 5.1	8.7 ± 1.3	0.6 ± 0.1	0.3 ± 0.13	n.d	4.0 ± 3.5	75.8 ± 3.4
E – Al/Fe phosphate	3	0.4 ± 0.3	1.7 ± 0.8	16.4 ± 1.2	29.9 ± 3.2	20.9 ± 2.3	2.4 ± 0.5	1.0 ± 0.7	1.6 ± 0.6	16.9 ± 3.4	91.3 ± 2.1
G - pure Al-P aggregates	6	0.5 ± 0.3	0.3 ± 0.4	15.0 ± 1.7	3.7 ± 3.4	31.7 ± 5.4	2.8 ± 0.4	0.8 ± 0.6	0.1 ± 0.0	2.0 ± 0.7	57.4 ± 4.0
H – Fe phosphate (not shown)	3	n.d	0.9 ± 0.5	11.1 ± 1.3	9.8 ± 1.7	28.5 ± 1.0	1.7 ± 0.7	0.8 ± 0.3	n.d	25.3 ± 2.6	78.8 ± 1.2
I - Bone apatite (not shown)	3	n.d	n.d	n.d	n.d.	43.7 ± 1.0	n.d.	52.9 ± 2.0	n.d	n.d	96.6 ± 1.2

The chemical composition for features G and H are similar to that reported for Taranakite ($(K, NH_4)_3Al_5H_6(PO_4)_{8x}18H_2O$) and Leucophosphite ($((NH_4K)_2(Fe, Al)_4(PO_4)_4(OHF)_{2x}2H_2O$), respectively (Tatur, 1989). However, K levels are lower than expected and might indicate that these are degraded phases of these minerals which have lost K. On the other hand, the low K values might be an indication that these minerals contain high proportions NH_4 in their structures. We observed crystalline Al phosphates resembling druses of variscite (Figure 12) and abundant nanometric amorphous Al-P minerals embebbed in a clayey mass (Figure 13).

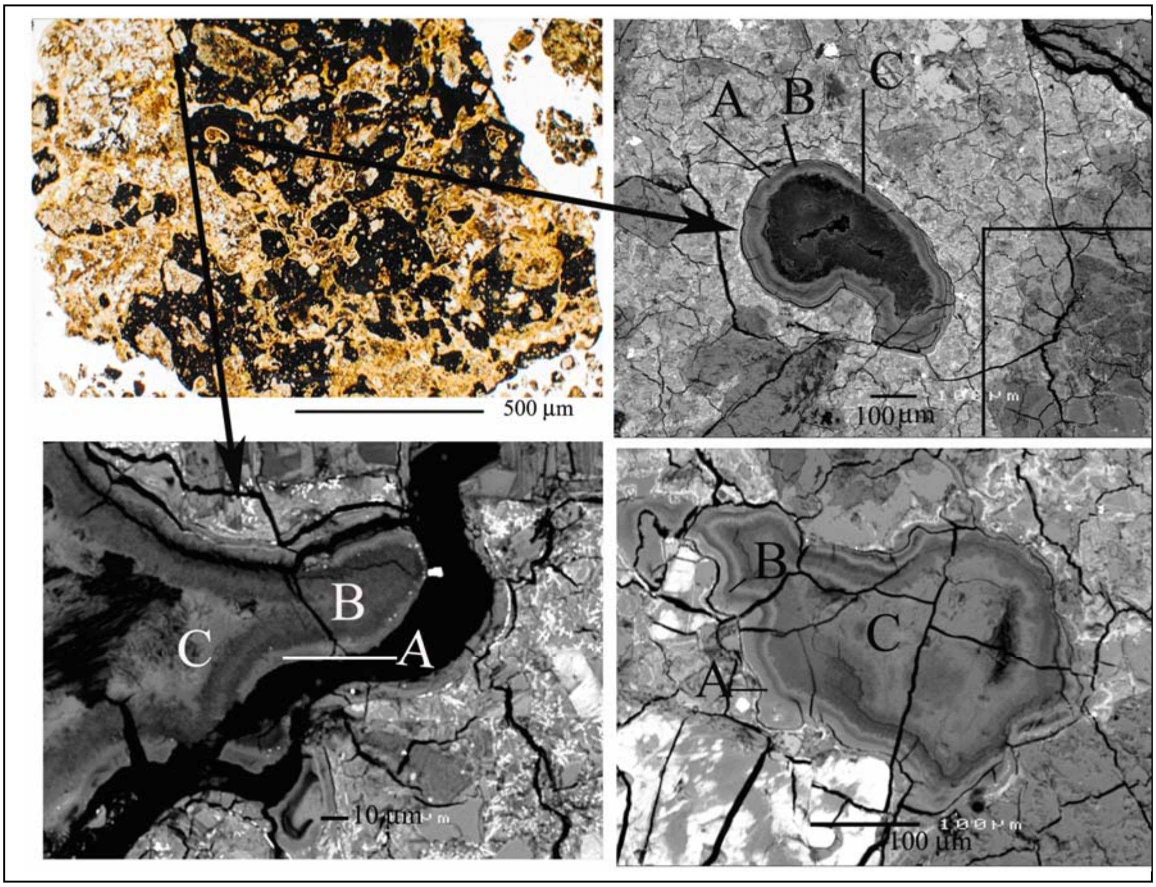

Figure 10 – Photomicrograph (top left) showing a highly phosphatized mafic clast with yellowish secondary illuvial phosphate filling dessication fractures and forming a complex framework of phosphatic rims. BSD images (top right and bottom) showing in detail the enclosure of glassy features by the yellowish illuvial phosphate. Quantitative EDS analysis show a progressive increase of P and Al with depletion of Si from the inner (C) to the outer part of the glass feature (A). The elemental map for portion indicated with the white square is presented in Figure 12.

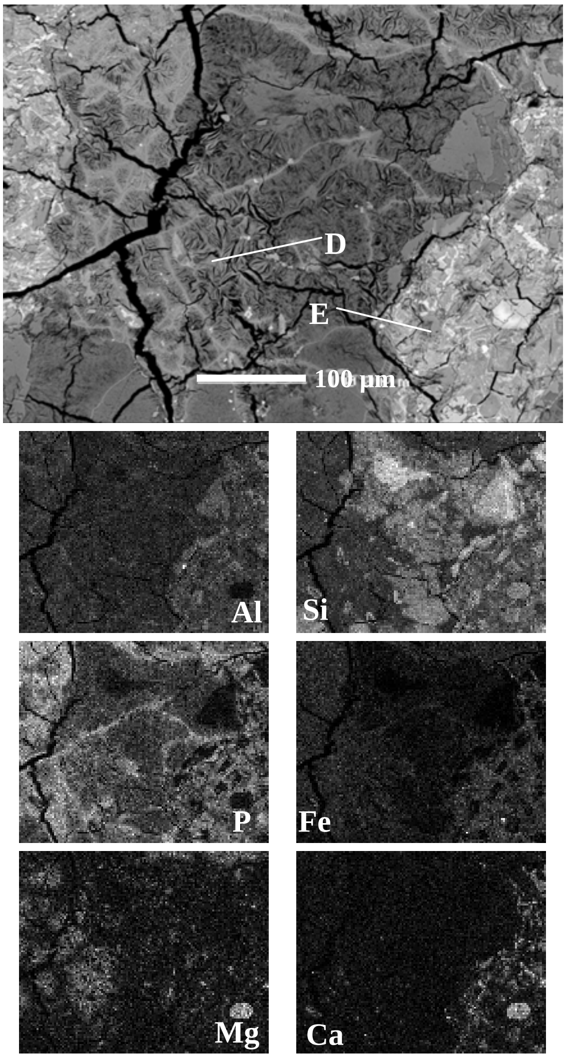

Figure 11 – BSD image and elemental maps (Al, Si, P, Fe, Mg and Ca) of the area indicated in Figure 11 showing the phosphatization of volcanic glass (D) with formation of Al phosphate with low Fe level (see also Table 4 –D) and (E) phosphatization of the mafic clast matrix with formation of Al/Fe phosphates (Table 4- E)

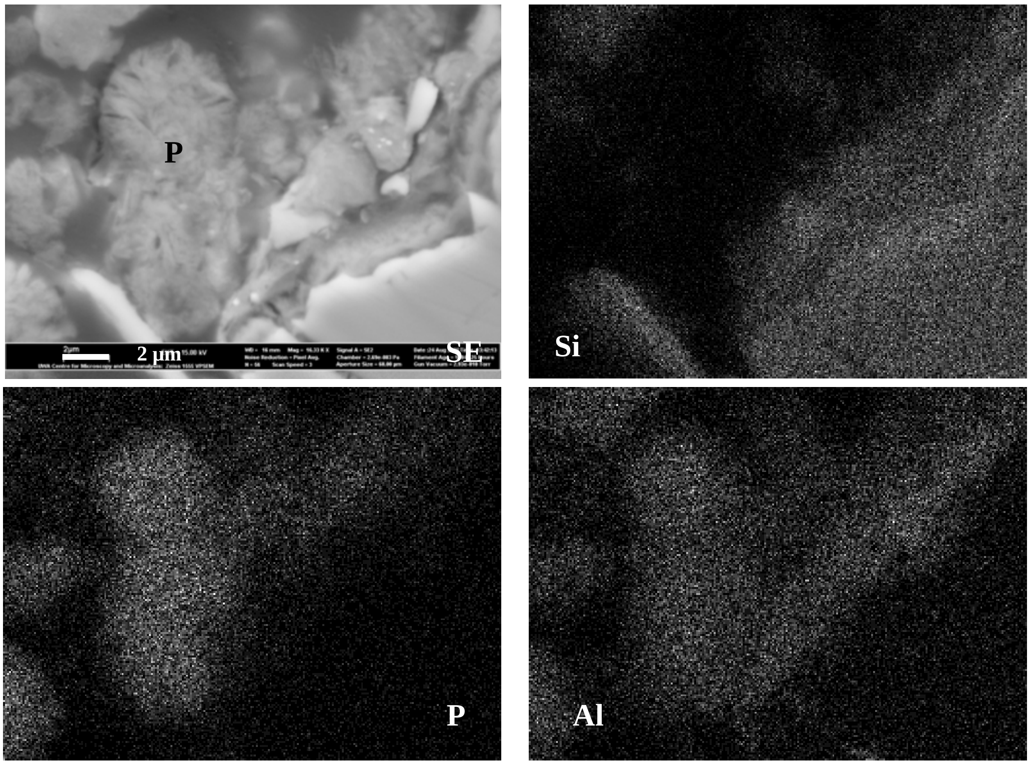

Figure 12 – Secondary electron (SE) image and elemental maps (Si, P and Al) showing pure Al-P aggregates (P) resembling druses of variscite as that shown in Tatur and Barczuk (1985).

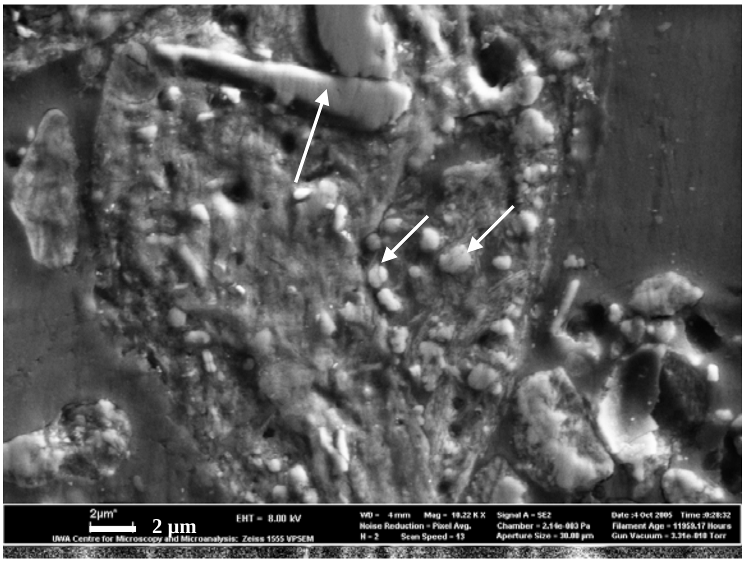

Figure 13 –SE image of amorphous Al phosphates (indicated by arrows) in a clayey matrix of an ornithogenic soils.

4. Conclusions

1. The fabrics of the studied soils are strongly influenced by the lithological fabric with high proportions of primary rock minerals in all size fractions. The subangular characteristics of sand–sized and coarser particles indicate short distance transport. The increasing roundness of lithorelicts with decreasing particle size reflects the effects of differential frost heaving and intense cryoturbation during freeze-and-thawing cycles.

2. The oxidation of sulphides is the most important process in acid sulphate soils and results in intense chemical transformation of soil minerals, with formation of jarosite and kaolinite. Jarosite forms illuvial coating within dessication fractures and is always associated with large amounts of amorphous Fe minerals with high P adsorption capacity.

3. The phosphatization process enhances chemical alteration of the substrate and is one of the main soil forming processes in ornithogenic soils. P-rich solutions penetrate dessication fractures and cleavage planes in large clasts and react preferably with volcanic glass but also with clasts groundmass. The reaction with P-rich solutions leads to the progressive displacement of Si from rock minerals. P reacts with Al and Fe to form various amorphous and crystalline P. Cryoclastic weathering and cryoturbation result in high levels of fine P-rich aggregates deep in the profile.

4 – Chemical weathering is much more important in Maritime Antarctica than previously thought, especially for acid sulphate and ornithogenic soils. The utilization of micromorphological and microchemical techniques proved to be extremely useful for a better understanding of pedogenesis in these poorly known soils.

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CAPÍTULO 5

Organic C stocks and humic fractions in Cryosols from Admiralty Bay, Maritime Antarctica

Abstract

Recent works show that organic matter accumulation in soils from coastal Antarctica is higher than previously expected. The objective of the present work was to investigate the distribution of soil organic matter (SOM) and humic fractions in ice-free areas of Admiralty Bay, King George Island, and estimate the organic C stocks for representative soils from this part of Maritime Antarctica. Ahumic Cryosols from subpolar desert landscapes presented the lowest organic C stocks. The establishment of cryptogamic plant communities increases soil C stocks, although these are lower than the values reported for most soils from polar areas. Ornithogenic influence results in C stocks comparable to those observed for Arctic tundra soils. The moss peat (with histic epipedon) presented the highest C stocks in Admiralty Bay (13.55 kg/m^2 considering a 100 cm depth), with levels similar to bog soils associated with coastal forests from Alaska. Most of the organic C in the studied soils is stored in the active layer but in the moss peat C it is also stored in the permafrost, increasing the potential emission after melting. SOM presents a low degree of humification and is largely composed by insoluble fragments inherited from poorly decomposed plant remains. Previous works suggest a high participation of biomacromolecules and N-rich humic substances in Antarctic Cryosols. Therefore, these soils can be considered highly vulnerable to C losses due to global warming.

Keywords: organic carbon, C stocks, Cryosols, Antarctica, humic substances, soils

1. Introduction

Permafrost-affected soils (Gelisols - SSSA, 2003 or Cryosols – ISSS, 1998) from Maritime Antarctica are different from those found in other parts of Antarctica (Campbell and Claridge, 1987; Blume et al., 2004). Warmer temperatures and higher water availability in this area result in deeper active layers and favor primary production and mineral weathering. Mosses and lichens form large communities at some sites, and a close relationship between faunal terrestrial activity and vegetation establishment is observed (Tatur et al., 1997; Michel et al., 2006). Intense faunal activity, especially by birds, results in the formation of ornithogenic soils (Ugolini, 1970; Ugolini, 1972; Campbell and Claridge, 1987; Tatur, 1989; Michel et al., 2006). According to Ugolini (1972), guano accumulation in penguin rookeries represents the most abundant source of organic matter in the Antarctic terrestrial ecosystem. At ornithogenic sites, the occurrence of the only two species of higher plants (*Deschampsia antarctica* Desv. (Poaceae) and *Colobanthus quitensis* (Kunth) Bartl. (Caryophyllaceae)) growing in Antarctica favor the formation of deep brownified soils.

Soil organic matter (SOM) is a key component of terrestrial ecosystems and its abundance and composition affect important ecological processes (Batjes, 1996). Soil organic carbon stocks are regulated by net primary production and SOM decomposition rates. Therefore, the study of organic C pools is essential for a better understanding of Antarctic terrestrial ecosystems in the current climate change scenario. According to Bockheim et al. (1999), C stocks in near-surface permafrost may be of global significance at high latitudes and should be inventoried. Increasing temperatures lead to permafrost melting and exposure of previously frozen organic materials, which may increase mineralization rates as verified for Arctic tundra soils (Ping et al., 1997). On the other hand, the retreat of Antarctic ice-sheets due to warmer temperatures exposes new mineral substrates to biological colonization and organic C incorporation, which may counteract the emissions.

Until recently, most soil data came from cold desert continental areas and that is probably the main reason why Antarctica is not considered in the world map of soil organic C distribution (Batjes, 1996). Recent studies show that organic matter accumulation in soils from coastal Antarctica are higher than previously expected (Blume and Bolter, 1993; Beyer et al., 1995; Jacobsen, 1997; Beyer, 2000; Beyer et al., 2004). However, studies on the origin and quality of Antarctic SOM are only beginning and should be considered a research priority which might be useful to understand more complex pedogenic processes under temperate and tropical climates (Beyer, 2004; Beyer et al., 2004).

The objective of the present work was to investigate the distribution of SOM and humific fractions in ice-free areas of Admiralty Bay, King George Island, and estimate the organic carbon stocks for representative soils from Maritime Antarctica.

2. Material and Methods

2.1 Study area

Admiralty Bay (62^{o}03’40”- 62^{o}05’40” S and 58^{o}23’30” - 58^{o}24’30” W) is located in King George Island, South Shetlands Archipelago, Maritime Antarctic. The location and general characteristics of this area have been described in the previous chapters.

2.2 Site characteristics and soil sampling

Based on previous studies (Tatur, 1989; Myrcha et al., 1991; Blume et al., 2004; Goryachkin et al., 2004; Chapters 1, 2 and 3) and field observations, we have grouped the soils from Admiralty Bay in the following groups, each with a distinct pattern of primary production and organic C incorporation: i) subpolar desert soils with sparse lichens and mosses; ii) poorly drained soils covered by mosses and lichens; iii) acid sulphate soils; (iv) soils under weak ornithogenic influence; v) ornithogenic soils from active penguin rookeries; vi) ornithogenic soils from abandoned penguin rookeries; vii) moss peats. Each of these groups represents a particular environment with distinct patterns of primary production and pedological characteristics which influence C sequestration in soils. Detailed data for these soils have been presented in the previous chapters.

Complete soil profiles and several surface samples were collected in all ice-free areas of Admiralty Bay (Figure 2). Discontinuous, ice-cemented permafrost was observed at 45 to 65 cm from the surface at the end of the austral summer, according to observations made from 2003 to 2005.

2.3 Chemical analyses and C stock calculation

Routine chemical and physical analysis were carried according to the methods described in Chapters 1 and 2. Humic fractions in < 0.5 mm soil samples were chemically fractionated based on their differential solubility in alkali and acid, according to Hayes et al. (1989). Table 1 shows the mean values for some chemical attributes for each soil group.

Carbon stocks for individual pedons were estimated according to Batjes (1996). The very high content of coarse rocky fragments made the bulk density (BD) determination by clod or core sampling impracticable. Therefore, the BD for the studied soils was estimated using the equation proposed by Bockheim et al. (1998) for Arctic tundra soils: $BD = (1.374)*10^{-0.26x}$ where BD = bulk density (g/cm^3) and x = organic matter content (%). The calculated C stocks were corrected for the content of > 0.5 mm fraction which was determined by dry sieving of bulk soil samples. The following equation was used for calculation of the carbon stock (Batjes, 1996):

$Cst = (TOC)*(BD)*(L.T.)*(1 - \% fragments>0.5mm)$, where:

Cst - carbon stock (Mg/m^2); TOC - total organic carbon (gC/gsoil), BD = bulk density (Mg/m^3) and L.T.= layer thickness (m).

The calculated bulk density values varied from 1.37 g/cm^3 for those horizons with very low organic C levels to 0.4 g/cm^3 for the moss peat (Table 2). Although this indirect determination is rather arbitrary the BD values obtained for the studied soils fall within the ranges reported for high latitude permafrost-affected soils (Batjes, 1996; Ping et al., 1997; Bocheim et al., 1999).

Carbon stocks were calculated from the sum of individual horizons for two depth intervals (0-30 cm and 0-100 cm) in order to enable comparisons with other studies (Batjes, 1996; Ping et al., 1997; Bockheim et al., 1999). When the soil was shallower than 100 cm, the C stocks obtained for the deepest layer were repeated until 100 cm.

3. Results and Discussion

3.1 Total organic carbon content and distribution

The data in Table 1 evidence the expected increase in soil TOC and N levels due to vegetation establishment. At the uppermost parts of the landscape, large desertic valleys with well drained soils have the lowest organic C content and negligible total N. These soils occupy the vast majority of ice-free areas from Admiralty Bay including unstable surfaces and scree slopes. Continuous moss communities colonizing similar soils along melting channels and fresh water ponds indicate that when enough water is available cryptogamic species are able to grow and TOC levels are slightly higher but not statistically different from the desert soils ($p < 0.05$ - Student's *t* test).

Bird guano is the most important source of P and N in Antarctic terrestrial ecosystems (Tatur et al., 1997). In the field one can readily identify areas affected by bird droppings from the presence of bird detritus, nest remains and exuberant vegetation with occurrence of flowering plants (*Deschampsia antarctica* and *Colobanthus quitensis*). Organic C and N levels increase significantly with ornithogenic influence and are highest for soils from abandoned penguin rookeries (Table 1). Although several studies have dealt with penguin breeding sites (Ugolini, 1970; Tatur, 1989; Tatur et al., 1997; Michel et al., 2006), very few have discussed the impacts of flying birds (skuas, giant petrels and sea gulls) on the development of terrestrial ecosystems. The data indicates that TOC levels for these soils can be considerably high (13.1±11.0 g/kg) for Antarctic standards.

Table 1 -Mean and standard deviation values of pH, extractable P, K and Na, exchangeable Ca, Mg and Al, total organic carbon (TOC) and total nitrogen for soils from different terrestrial environments of Admiralty Bay.

Soil type	n	pH	P^1	K^1	Na^1	$^2Ca^{2+}$	$^2Mg^{2+}$	$^2Al^{3+}$	COT	N	> 2 mm	sand	silt	clay
		H_2O	mg/dm^3			cmol$_c$/dm^3			g/kg		%			
Basaltic/andesitic	86	7.4 ± 0.6	266.4 ± 163.6	83.5 ± 45.0	225.8 ± 242.4	24.6 ±15.5	7.2 ±11.6	0.06 ± 0.2	3.5 ± 5.1	n.d.	30 - 86	38 ± 16	32 ±7	25 ± 5
Acid sulphate	16	4.9 ± 0.5	39.7 ± 25.8	55.2 ± 32.8	117.2 ± 47.4	10.1 ± 6.1	5.0 ± 4.5	14.5 ± 13.4	5.0 ± 8.4	n.d.	9 - 68	41 ± 23	45 ± 19	5.8 ± 5.1
Weak ornithogenis	73	6.3 ± 0.8	252.4 ± 151.8	291.8 ± 258.8	202.9 ± 104.5	13.1 ± 7.3	6.4 ± 5.6	1.4 ± 3.4	12.2 ± 12.8	2.7 ± 3.0	16 - 73	41 ± 18	32 ±4	21 ±8
ornithogenic soils	41	4.1 ± 0.3	1356.7 ± 956..3	856.6 ± 293.6	372.0 ± 254.7	4.7 ± 5.6	1.5 ± 2.5	7.1 ± 3.4	32.0 ± 29.0	4.3 ± 1.0	18 - 95	73 ± 10	15 ± 7	11 ± 4

[1] - extracted with Melich-1; [2] - extracted with 1 mol/L KCl;[3] total organic C and total N; n - number of horizons analyzed; n.d – not detected.

In order to detail the vertical distribution and stocks of organic C within the soil profile, a few pedons were chosen to represent each soil group (Table 2). Soils covered exclusively by cryptogamic species (pedons K13 and K21) show an abrupt decrease in TOC values at depth. On the other hand, those soils supporting flowering plants (pedons K20, K23, A3 and A5) have a more gradual decrease and normally maintain relatively high TOC values at depth (Table 2). Pedons under "weak" ornithogenic influence (pedon K20 and K23) have similar and even higher TOC levels than those under *strong* ornithogenenis (pedons A6, A3, A5). The moss peat had the highest C levels with depth (Table 2).

Primary production as a role is increased in ornithogenic sites with the formation of exuberant moss carpets. At well-drained sites, moss communities are gradually overgrown by the two higher plants which use the decaying moss as a substrate. This is more notable for *D. antarctica* which frequently forms continue grass fields. A well-developed root system forms a dense network in the A horizon and roots are also common in the deeper soil layers resulting in the higher TOC values with depth. It has been recently shown that root-derived organic C has in average a 2.4 times higher residence time in soils than shoot-derived organic C and that the contribution of the root system to stabilizing soil organic matter is greater than that of the aerial parts (Rasse et al., 2005).

Table 2 – Total organic C (TOC), bulk density and percentage of > 0.5mm particles for the selected pedons (means of three replicates).

Depth (cm)	T.O.C. g/kg)	BD (g/cm^3)	>0.5mm particles (%)
Subpolar desert			
Pedon K16 -Typic Haploturbel			
0-70	1.0	1.3	55.9
Pedon A10 - Typic Psamoturbel			
0-70	1.0	1.3	82.9
Cryptogamic vegetation			
Pedon K13 - Typic Haploturbel			
0-10	41.0	0.5	97.1
10-20	5.0	1.2	97.1
20-60	2.0	1.3	92.8
Pedon K21 - Lithic Haploturbel			
0-10	9.0	1.1	98.1
10-50	2.0	1.3	94.7
Acid sulphate soil			
Pedon K24 - Sulphuric Haploturbel			
0-10	5.0	1.2	60
10-20	2.0	1.3	25
20-60	1.0	1.3	46
Weak ornithogenic influence			
Pedon K20 - Typic Umbriturbel			
0-10	65.0	0.3	95.7
10-20	19.0	0.8	95.9
20-50	7.0	1.2	88.4
Pedon K23 - Typic Umbriturbel			
0-10	36.0	0.5	95.1
10-30	21.0	0.8	90.3
30-40	12.0	1.0	96.0
40-50	7.0	1.2	95.7
50-60	3.0	1.3	97.9
Active penguin rookery			
Pedon A5 - Ornithogenic Haploturbel			
10-20	26.0	0.7	94.4
20-30	7.0	1.2	97.5
Abandoned penguin rookery			
Pedon A3 - Ornithogenic Psammoturbel			
0-10	15.0	0.9	99.0
10-20	8.0	1.1	99.4
20-70	13.0	1.0	97.1
Pedon A6 – Ornithogenic Umbriturbel			
0-10	24.0	0.7	95.9
10-20	20.0	0.8	96.5
30-50	13.0	1.0	93.0
Moss Peat			
Pedon A7 - Ornithogenic Fibristel			
0-10	44.0	0.4	97.1
10-20	35.0	0.6	96.4
20-30	22.0	0.8	96.4
30-70	31.0	0.6	85.7
70-80	21.0	0.8	96.4

3.2 Organic C stocks

The estimated organic C stocks at different depths for the selected pedons are presented in Table 3. The total stocks in each pedon, considering the depth of the solumm, ranged from 0.3 to 7.0 kg/m^2 for the mineral soils and reached 11.1 kg/m^2 in the organic soil (pedon A7). Michel (2006) reported similar ranges for nearby soils in the vicinities of Llano Point (0.1 to 9.0 kg/m^2), in Admiralty Bay. These values are also within the ranges presented by Beyer et al. (2004) for soils near Casey Station (0.3 to 8.2 kg/m^2 for mineral soils, and 5.2 to 45.6 kg/m^2 for Gelic Histosols). Compared to the Artic region, the estimated C stocks for soils from Admiralty Bay at 100 cm depth (Table 3), are low in relation to the range reported by Bockheim et al. (1999) for tundra soils (2.5 to 75.2 kg/m^2) and much lower than those reported by Ping et al. (1997) for coastal marsh and forest soils (69.2 kg/m^2 and 78.7 kg/m^2, respectively).

As expected, subpolar desert soils had the lowest stocks (Table 3). For both depth ranges (0-30 and 0-100 cm), the estimated C stocks for pedons K16 and A10 (Table 3) were lower than the global mean reported by Batjes (1996) for world soils (0.8 to 40.6 kg/m^2 for 30 cm, and 3.1 kg/m^2 to 77.6 kg/m^2 for 100 cm). Therefore, these ahumic cryosols from Antarctica are probably amongst the soils with the lowest C content in the planet. Although slightly higher, the organic C stocks estimated for soils under cryptogamic vegetation (Table 3 – pedons K13 and K21) are also low in relation to most soil classes in the world (Batjes, 1996) and similar to those estimated some soils from eastern Antarctica (Beyer et al., 2004).

The activity of skuas and other flying birds resulted in a considerable increase in the C stocks (4.7 and 7.0 kg/m^2, for pedons K20 and K23 respectively). These values are comparable to those obtained for soils from active and abandoned rookeries (pedons A6, A3 and A5) and to mineral soils from coastal eastern Antarctica (Beyer et al., 200). Despite their limited geographic expression, nesting sites of skuas, giant petrels and sea-gulls are important C sinks in Antarctica. Until now, the impacts of these birds in terrestrial ecosystem had received almost no scientific interest since most studies have concentrated in penguin rookeries.

The Ornithogenic Fibristel (pedon A7) from the moss peat had the highest C stock from all pedons studied in the present work (13.55 kg/m^2, at 100 cm depth). This value is much lower than the global mean value reported for Histosols (72 – 125 kg/m^2 , Batjes, 1996) and falls at the lower end of the range reported by Beyer et al. (2004) for Histels from coastal eastern Antarctica (5.2 to 45.6 kg/m^2). In pedon A7, more than 60 % of the stored organic C is located deeper than 30 cm indicating that great part of the organic C is located in the permafrost. Therefore, similarly to some Arctic soils climate change may change organic soils in Antarctica from a carbon sink to a source of C emission (Oechel et al., 1993; Ping et al., 1997; Bockheim et al., 1999).

Besides the organic C levels, which are notably increased by the ornithogenic influence, variations in the coarse particles content in soils also determine total C stocks estimates. In the present study, both pedons from the Psammoturbel great group (pedons A10 and A3) presented the lowest C stocks when compared to Haploturbels from similar environments (Table 3). Due to the coarse texture, the Psammoturbel from the abandoned penguin rookery (pedon A6) had lower C stocks than the acid sulphate soil (pedon K24) despite the much higher TOC levels in the < 0.5mm fraction for A6. The acid sulphate soil had the lowest amount of particle > 0.5 mm and, therefore, presented a quite high C stock considering the relatively low organic C content. This is also valid for some basaltic/andesitic soils such as pedon K16.

Table 3 – Estimated C stocks for the selected pedons at different depths.

Soil	Depth	Total C stock [1]	0-100 cm	0-30 cm
	cm	kg/m^2		
Subpolar desert				
K16 –Typic Haploturbel	70	1.11	1.59	0.47
A10 –Typic Psamoturbel	70	0.33	0.48	0.14
Cryptogamic vegetation				
K13 - Typic Haploturbel	60	2.00	2.42	1.70
K21 - Typic Haploturbel	50	0.64	0.96	0.51
Acid sulphate soil				
K24 - Sulphuric Haploturbel	60	2.30	2.97	1.79
Weak ornithogenic influence				
K20 - Typic Umbriturbel	50	4.65	7.79	3.40
K23 - Typic Umbriturbel	60	7.04	7.50	4.67
Active penguin rookery				
A5 - Ornithogenic Haploturbel	30	2.38	5.52	2.38
Abandoned penguin rookery				
A3 - Ornithogenic Psammoturbel	70	1.17	1.64	0.55
A6 - Ornithogenic Umbriturbel	50	4.53	9.09	3.63
Moss Peat				
A7 - Ornithogenic Fibristel	70	11.06	13.55	4.15

[1] - Total organic C stock considering the real depth of each the pedon

3.3 Humic substances

The results of the humic substances fractionation for some soils from Admiralty Bay are presented in Table 4. The high organic C recover by the fractionation (Rec = 105 ± 9 %) in relation to the total organic carbon indicates that nearly all organic C forms in the samples were efficiently measured.

The non-extractable organic matter (NEOM) accounted for 44.6 to 83.7 % of the humic fractions in the studied pedons. Pedons A10 and A5 had the highest values (66.7 to 82.0 %), whereas for pedons A3 and A5 this value ranged from 44.6 to 57.7 %. At high latitudes, soils with ice-cemented permafrost experience extreme cold and temporary water saturation which retard the complete decay of plant remains (Stevenson, 1994; Andreux, 1996; Saiz-Jimenez, 1996). Poorly transformed materials normally yield low proportions of extractable compounds (Andreux, 1996). Therefore, the high levels of non-extractable organic matter for some samples in the present study (Table 4) can be partially due to incompletely mineralized, fibric plant remains (Michel et al., 2006).

Although the insoluble fraction is methodologically defined as humin, poorly decomposed non-humic insoluble organic residues are not be chemically defined as humic substances and should not be confused with humin (Hayes and Malcolm, 2001). Hence, we have followed the nomenclature proposed in Michel et al. (2006) and used the term non-extractable organic matter (NEOM) when referring to the insoluble fraction of soils from Admiralty Bay.

Contrasts in the vertical distribution and proportions of humic (HAF) and fulvic acid fractions (FAF) for the different pedons were also observed (Table 4). In general terms, the HAF/FAF in soils is expected to increase with the transformation degree of SOM, reflecting the higher degree of polymerization of HAF (Andreux, 1996).

In the present study, the lowest HAF/FAF was obtained for pedon K10 which is in fact the youngest of the four soils studied. It is located in a basaltic/andesitic, stable cryoplanation surface at approximately 200 m a.s.l., close to the glacier front, being covered exclusively by cryptogams. The moss residues have not suffered much transformation is this young soil which also presented the highest proportion of NEOM as indicated by the lowest (HAF + FAF)/NEOM ratio (0.4) (Table 4).

For pedon A5, a decrease of the HAF/FAF ratio with depth is observed and is attributed to the higher mobility of the FAF. The reduction of the (HAF + FAF)/NEOM ratio with depth indicates that the soluble fractions are concentrated in the surface layers where biological activity and deposition of plant residues are highest. This might be due to a more recent colonization by plants and predominance of cryptogams in relation to higher plants combined with a lower degree of cryoturbation.

On the other hand, for pedon A7 a slight increase in the (HAF + FAF)/NEOM ratio, TOC, HAF and FAF values at depth indicate that SOM is migrating and accumulating at and within the permafrost, characterizing an incipient podzolization process. The increase in the HAF/FAF ratio suggests polymerization of FAF with depth with formation of more policondensed, recalcitrant compounds. This is favored by the exuberant plant cover observed in this soil which continuously releases organic compounds and also by the high activity of Al which forms stable complexes with organic compounds. Similar results have been reported for other ornithogenic soils from Admiralty Bay (Michel et al., 2006).

For pedon A3, uniform values of HAF/FAF and (HAF + FAF)/NEOM ratios for all depths suggest high preservation of soluble fractions throughout the profile. The relatively high HAF/FAF suggest a higher degree of soil development for pedons A3 and A7 in relation to the other two pedons studied in the present paper.

The type of vegetation cover determines the quality of SOM (Stevenson, 1994). Polyols, monossaccharides, polyssacharides, proteins, amino acids, carotenoids and vitamins are present in lichens (Saiz-Kimenez, 1996). Mosses have similar chemical constituents as higher plants including polyssacharides, proteins, lipids and carotenoids although the presence of lignin is doubtful (Saiz-Kimenez, 1996). According to Chopra and Kumra (1988), algaenan and lignin-like materials are present in some mosses. At cold, wet regions, the slow rates of decomposition increase the preservation potencial of all macromolecules which may act as humic substances precursors (Stevenson, 1982). The formation of humic substances in such environments where lignin and lignin-degradation products are not prevalent can occur through the condensation of sugar-amine compounds, or reactions between quinones and amino-acids (Beyer et al., 1995).

There are very few works about the qualitative aspects of soil organic matter (SOM) and humic substances in Antarctic soils (Beyer et al., 1995; Beyer, 2004, Beyer et al., 2004; Michel et al., 2006). Although mosses constitute the most important source of organic matter for most soils in Antarctica, lignine-bearing flowering plants are also important at well-drained ornithogenic sites. Beyer et al. (1995, 2004a), studying organic soils from Wilkes Land, East Antarctica, found that the SOM in Histels formed from moss accumulation consisted mainly of carbohydrates and lipid-derived compounds. They also found indications that aromatic lignins are not necessary for the formation of aromatic humic substances. Many different reactions can form humic substances in soils including reactions involving microbially produced polyphenols and quinones and polymerization with amino-acids (Stevenson, 1994). Michel et al., (2006) studying purified humic acids from ornithogenic soils of Admiralty Bay found high proportions of N and easily thermodegradable compounds.

Table 4 – Total and relative non-extractable organic matter (NEOM), humic acid (HAF) and fulvic acid (FAF) fractions for some pedons from Admiralty Bay.

Depth	**NEOM**	**HAF**	**FAF**	**Sum[1]**	**TOC[2]**	**Rec[3]**	**NEOM**	**HAF**	**FAF**	**HAF/FAF**	**(HAF+FAF)/H**
cm	**g/kg**					**%**					
Soil with cryptogamic vegetation Pedon K10 – Lithic Haploturbel											
0-10	26.9	1.5	4.3	32.7	28.9	113.1	82.3	4.6	13.1	0.4	0.2
Ornithogenic soils from abandoned rookeries Pedon A4 – Ornithogenic Psammoturbel											
0-10	24.1	9.2	8.9	42.1	15.0	280,7	57.2	21.9	21.1	1.0	0.8
10-20	9.3	4.9	5.3	19.6	8.0	245,0	47.4	25.0	27.0	0.9	1.1
20-30	7.5	2.7	3.5	13.7	14.0	97,9	54.7	19.7	25.5	0.8	0.8
40-50	7.7	2.7	3.2	13.6	13.0	104,6	56.6	19.9	23.5	0.8	0.8
50-60	8.3	2.9	3.6	14.8	14.0	105,7	56.1	19.6	24.3	0.8	0.8
60-70	7.6	2.9	3.2	13.7	13.0	105,4	55.5	21.2	23.4	0.9	0.8
Pedon A6 – Ornithogenic Umbriturbel											
0-10	16.6	3.6	4.7	24.9	24.0	103,8	66.7	14.5	18.9	0.8	0.5
10-20	16.9	2.9	3.3	23.1	20.0	115,5	73.2	12.6	14.3	0.9	0.4
20-30	9.5	1.0	1.4	12.0	13.0	92,3	79.2	8.3	11.7	0.7	0.3
30-40	11.3	0.8	1.5	13.5	13.0	103,8	83.7	5.9	11.1	0.5	0.2
Moss peat **Pedon A7 – Ornithogenic Fibristel**											
0-10	24.5	10.4	12.9	47.8	44.2	108,1	51.3	21.8	27.0	0.8	1.0
10-20	22.3	8.4	10.3	40.9	35.0	116,9	54.5	20.5	25.2	0.8	0.8
20-30	15.0	6.2	6.3	27.5	22.0	125,0	54.5	22.5	22.9	1.0	0.8
30-40	13.3	8.3	6.9	28.5	29.0	98,3	46.7	29.1	24.2	1.2	1.1
40-50	14.0	9.7	7.7	31.4	32.0	98,1	44.6	30.9	24.5	1.3	1.2
50-70	14.6	9.5	7.8	31.9	21.0	151,9	45.8	29.8	24.5	1.2	1.2

[1] (NEOM+HAF+FAF); [2]total oganic C; [3]Sum/TOC

4. Conclusions

1. Ice-free areas of Admiralty Bay are formed mainly by subpolar desert soils with very low C stocks. The establishment of cryptogamic communities occurs at humid sites but soil C stocks are still lower than that found for most soils from high latitudes.

2. Despite their reduced geographic expression, ornithogenic soils are without doubts the most important compartment of immobilized C in ice-free areas Admiralty Bay. The presence of higher plants at these sites, with well developed root systems, coincides with higher organic C levels with depth. These are highest for poorly drained sites where moss peats have formed and over 60 % of the organic C stock is stored in the permafrost layer. Eventual global warming and permafrost degradation may change these sites from C sinks to sources.

3. Sites under the influence of flying birds may have total organic C levels and stocks comparable to those observed in areas under much stronger influence by penguins and should be studied in more detail.

4.The degree of SOM humification is largely determined by the age and type of the vegetation cover with higher levels of extractable fraction occurring at deeper, more developed soils with exuberant plant cover. In Maritime Antarctica, the high water availability promotes percolation of organic compounds in the profile and incipient podzolization. The characterization of the different organic compartments for soils with and without higher plants is crucial for a better understanding of organic C dynamics in this part of Antarctica and may reveal important information for a better understanding of humification mechanisms at lower latitudes.

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CAPÍTULO 6

Bioaccumulation of heavy metals in lichens, mosses and flowering plants from Admiralty Bay, Maritime Antarctica: environmental indicators

Abstract

There is a growing scientific concern regarding the monitoring of environmental impacts in Antarctica. Lichens, mosses and higher plants are potential bioindicators for studying the levels and spatial distribution of anthropogenic pollutants. In this work, we have studied the total levels of several macro and micronutrients, including some heavy metals in different species of lichens (*Usnea spp.* and *Sphaerophilous globosus*), mosses (*Sanionia uncinata* and *Polytrichales sp.*) and flowering plants (*Deschampsia antarctica* and *Colobanthus quitensis*) from Admiralty Bay, Maritime Antarctica. Low levels of Cd, As, Cr, Ni and Pb for all studied organisms in relation to other remote areas suggest negligible contamination by anthropogenic emissions. Element levels for mosses and *D. antarctica* reflect local geochemical characteristics while the composition of *Usnea* is less affected by substrate variations. Higher Cd levels in *Deschampsia* a*ntarctica* and mosses from ornithogenic sites suggest that these may be useful for monitoring heavy metal sea-land transference along Antarctic food webs. Due to the highly variable levels for all elements and all organisms studied, it is necessary to establish permanent monitoring sites to avoid misinterpretations and inadequate comparisons of element levels in eventual monitoring schemes..

Keywords: bioaccumulation, heavy metals, Antarctica, mosses, lichens, *Deschampsia antarctica*, ornithogenesis.

1. Introduction

Antarctic ecosystems are known for their high sensitivity to anthropogenic contaminants and there is a growing scientific concern regarding the development of environmental impact monitoring strategies for these areas (Honda et al., 1987). In this regard, the use of bioindicators is a common approach for assessing the occurrence, concentration, bioavailability and distribution of contaminants in the environment (Bargagli, 1995; Poblet et al., 1997; Bargagli et al., 1998; Mertens et al., 2005). However, this depends on the definition of background levels for pollutants in the environment (air, water, soil) and in the biota (Conti and Cecchetti, 2001). Once correctly established, the background level can be assumed as the natural level of a given contaminant, for a certain specie or group, and can be used as a reference for monitoring anthropogenic impacts.

Terrestrial ecosystems of maritime Antarctica are more complex than those observed on dryer and colder continental Antarctica. Warmer temperatures and higher rainfall result in greater soil development and enhanced primary production (Ugolini, 1970; Campbell and Claridge, 1987; Michel et al., 2006). Vegetation communities are composed mainly by lichens and mosses but, differently from other parts of Antarctica, two flowering plants are present (*Deschampsia antarctica* Desv. (Poaceae) and *Colobanthus quitensis* (Kunth) Bartl. (Caryophyllaceae)).

The *Usnea* species (*U. antarctica* and *U. aurantiacoatra*) are the most common epilithic lichens in maritime Antarctica (Poblet et al., 1997), colonizing a wide range of terrestrial environments. At the uppermost areas, *Usnea* grows on rock outcrops, boulders and rock fragments at the soil surface. At lower areas, it grows along with mosses and higher plants forming more complex communities. Mosses grow preferably at more protected, wetter sites along melting water channels and around lakes and small ponds.

Sanionia uncinata (Hedw.) Loeske forms extensive green carpets, while the *Polytrichales* species occur as small tuffs, being abundant around bird nesting areas.

The two flowering plants are common at well-drained soils which were affected by faunal activity. Initial or weak ornithogenic sites occur in all ice-free areas of Admiralty Bay usually as small, disconnected areas around nesting sites of flying birds (skuas, petrels and sea-gulls). Nevertheless vegetation development is notably enhanced. The largest ornithogenic areas occur in the vicinities of penguin rookeries and are restricted to the western coast, which is the oldest ice-free area at Admiralty Bay.

Several authors have proposed the use of epilithic lichens for monitoring heavy metal air-borne deposition in Antarctica (Bargagli, 1989; Bargagli and Focardi, 1992; Poblet et al., 1994; Poblet et al., 1997). On the other hand, others have studied heavy metal and nutrient accumulation in mosses (Bargagli et al., 1995; Bargagli et al., 1998), and in flowering plants (Tatur et al., 1997; Albuquerque-Filho, 2005).

In this work, we have studied the total levels of several nutrients and heavy metals in different species of lichens (*Usnea sp.* and *Sphaerophilous globosus*), mosses (*Sanionia uncinata* and *Polytrichales sp.*) and flowering plants (*Deschampsia Antarctica* and *Colobanthus quitensis*) from ice-free areas of Maritime Antarctica. The main objective is to contribute to the identification of appropriate bioindicator(s) and the establishment of background values for future monitoring.

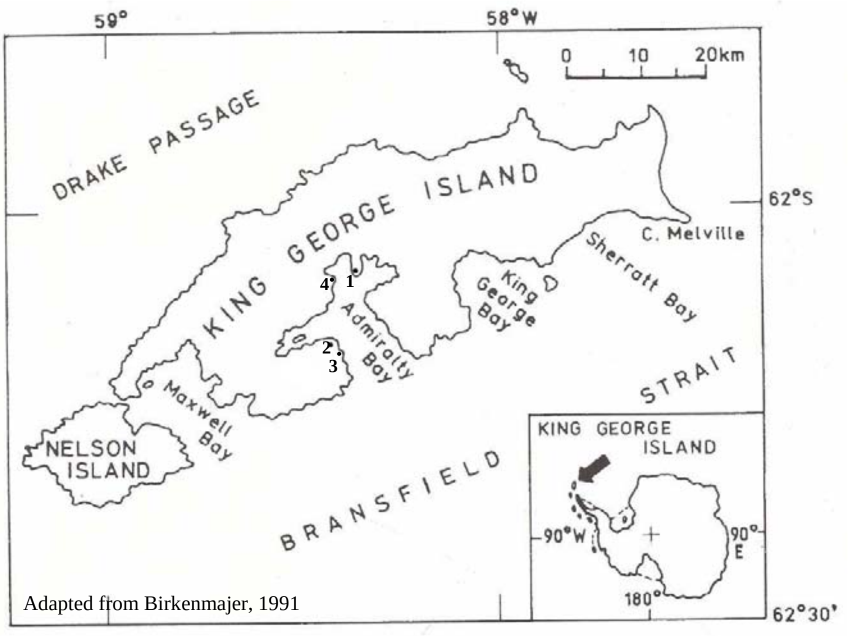
2. Material and methods

2.1 Study area

The Admiralty Bay (62^{o}03’40”-62^{o}05’40” S and 58^{o}23’30”-58^{o}24’30” W) is located in King George Island and is part of the South Shetlands Archipelago, Maritime Antarctica (Figure 1). Several scientific stations are located in Admiralty Bay (Figure 1).

Data sets from 1982-2002 acquired at the Brazilian Comandante Ferraz Station report mean air temperatures varying from -6.4 ^{o}C in July to + 2.3 ^{o}C in February. Mean annual precipitation is 366.7 mm. Positive air temperatures occur from November until March when effective precipitation as liquid water is increased due to melting of accumulated winter snow.

1
1



Adapted from Birkenmajer, 1991

Figure 1 – Location of Admiralty Bay in King George, maritime Antarctica and approximate position of scientific stations. 1- Comandante Ferraz (Brazil); 2- Henry Arctowski (Poland); 3. Peter Lennie (USA); Machu Picchu (Peru).

2.2 Soils

Vegetation communities from ice-free areas of Admiralty Bay develop on two geochemically contrasting substrates and related moraine, solifluction and fluvioglacial deposits: (i) basaltic/andesitic soils (most of the ice-free area) and (ii) acid sulphate soils derived from sulphide-bearing andesites. The continuous deposition of P and N-rich guano by Antarctic birds leads to the formation of unique acid soils with high C and P levels (Tatur and Barzuk, 1985; Tatur, 1989; Michel et al., 2006). At abandoned penguin rookeries, the clay fraction mineralogy of these so-called *ornithogenic* soils (Tatur, 1989) is composed mainly by crystalline and amorphous P minerals, resulting in anomalously high P bioavailability.

2.3 Sampling

During the summers of 2003/2004 and 2004/2005, 46 samples of lichens (44 samples of *Usnea spp.* and 2 of *Sphaerophilous globosus*), 63 samples of mosses (50 of *Sanionia sp* and 13 of *Politrichales sp.*) and 34 samples of flowering plants (20 of *Deschampsia antarctica* and 14 *Colobanthus quitensis*) were collected on all ice-free areas of Admiralty Bay. At each site, samples were collected by mixing several specimens of a given vegetation type to form one composite sample. This procedure was done in three replicates for each vegetation type.

Sites were carefully chosen in order to represent the main environmental variations (i.e. basaltic soils, acid sulphate soils and ornithogenic sites). Soil samples from all sites were also collected and submitted to detailed chemical and mineralogical characterization (Chapters 1, 2, 3 and 4; Albuquerque-Filho, 2005). Some general characteristics of the sampled sites are summarized in Table 1.

2.4 Chemical extractions

Unwashed plant samples were carefully separated and cleaned from all visible soil contamination, dried at 60^{o} C until constant weight, grounded and submitted to a nitro-perchloric digestion (concentrated HNO_3 + $HClO_4$ at 180 ^{o}C for 4 hours) as described by Malavolta et. al. (1989). In the extracts, total levels of Al, Ca, Mg, Fe, Ti, Mn, Cu, Ba, Sr, Ni, Cd, Cr, As, Mo, Pb, Se, V and Zn were determined by inductive coupled plasma emission spectrometry; K determined by flame absorption photospectrometry and; P determined by photocolorimetry. Air-dried < 2mm soil samples were submitted to routine chemical extractions (EMBRAPA, 1997) which are described in more details by in Chapter 1. The total organic carbon content was determined for < 0.5 mm samples by wet combustion (Yeomans and Breemen, 1988) and total nitrogen was determined by the Kjeldahl method (EMBRAPA, 1997).

2.5 Statistical analysis

Differences in element concentration in the samples were tested using Student's *t* test at a probability level of <0.05. The correlation coefficient between elements in plants and corresponding substrates were also calculated. All statistical analyses were made using the Statistica$^{@}$ software.

Table 1 – Some chemical characteristics of the main soil types from Admiralty Bay.

Substrate	n	pH	P[1]	Ca[2]	Mg[2]	Al[2]	Total Fe[3]	Total Al[3]	TOC[4]	N[5]
		H_2O	mg/dm^3	cmol$_c$/dm^3			%			
Basaltic/andesitic soils	75	7.3 ±0.63	272.8 ±173.4	25.4 ±16.1	7.7±12..5	0.06 ±0.25	2- 4.5	1.3-4.0	0.28±0.45	n.d.
Acid sulphate soils	20	5.4 ± 1.0	132.0±152.9	14.4± 8.4	5.4±3.9	11.5±3.4	4.0–>7.0	2.0 – 4.5	0.43±0.67	n.d.
soils under weak ornithogenic influence	91	6.4±0.9	227.9±159.0	13.8±7.8	5.8±5.2	2.8±7.0	-	-	1.03±1.19	0.27±0.3
ornithogenic soils from active penguin rookeries influence	3	4.0±0.4	2516.5±1522.5	10.0±2.8	2.5±1.1	9.5±4.0	-	-	1.31±1.10	0.43±0.1
ornithogenic soils from abandoned penguin rookeries	32	4.2±0.3	1409.6±935.6	4.9±6.3	1.6±2.9	6.3±3.0	-	-	3.56±3.30	0.39±0.2

[1] P extracted with Melich-1 (bioavailable P); [2]exchangeable cations; [3] Total Fe and Al (Albuquerque-Filho, 2005); [4] Total organic carbon (TOC); [5] Total Nitrogen.

3. Results and Discussion

The results of the total elemental analyses for each group are summarized in Table 2. The levels of As, Mo and Se were below the detection limits for all samples and are not presented. High coefficients of variation were obtained for all elements and plant materials. This has been previously reported for Antarctic plants (Bargagli, 1995), and is attributed mainly to the contamination by different amounts of soil dust. In maritime Antarctica, site-specific, pedo-geochemical variations affect element bioavailability (Albuquerque-Filho, 2005) and are likely to contribute for the high standard deviations observed (Table 2).

Despite relatively high variation coefficients, significant differences in elemental levels for the different vegetation groups (mosses, lichens and flowering plants) were observed, as follows.

3.1 Mosses (*Sanionia uncinata* and *Polytrichales sp.*)

Bryophites are known for their capacity to accumulate heavy metals and other persistent atmospheric contaminants (Bargagli et al., 1998). Similarly to lichens, these cryptogamic organisms lack proper roots and waxy cuticles and depend partially on atmospheric deposits for their nutrients (Bargagli et al., 1998). Therefore their elemental composition reflects the availability of a gaseous, dissolved and particultate elements is air, snow and melting water (Bargagli et al., 1998). There are very few studies on the accumulation of nutrients and heavy metals by Antarctic mosses (Bargagli et al., 1995), notably for maritime Antarctica (Yurukova and Ganeva, 1999).

Sanionia uncinata and *Polytrichales sp.* are very frequent in plant communities from different areas of maritime Antarctica (Putzke and Pereira, 1990; Pereira and Putzke, 1994; Ochyra, 1998; Putzke and Pereira, 2001; Ochyra et al., 2000). Therefore they are potential indicators for monitoring metal deposition and bioavailability in this part of the continent. We have found no significant differences in the studied elements for the two moss species except for P, which is significantly higher in samples of *Sanionia uncinata* (Table 2). This moss is typically found in ornithogenic areas, rich in P (Michel et al., 2006).

In general, mosses presented significantly higher levels of Al, Fe, Mg, Ti, Cu, and V than the higher plants (Table 2). When compared to lichens, the levels of K, P, Mn, Ni and Ba were also significantly higher. Anomalously high and extremely variable levels of Al (0.1-3.4%) and Fe (0.1-4.8 %) in relation to mosses from the nearby Livingstone Island (0.15-0.35 % of Fe – Yurukova and Ganeva, 1999); and from continental Antarctica (0.11-0.72 % for Al and 0.14-0.82 % for Fe, Bargagli et al., 1998) were observed. This might be due to contamination by soil dust as suggested by the highly significant positive relationships between the levels of geochemically related elements (Fe, Al, Ca, Mg, Mn, Cu, Ba, Ti, Cu, Ni, V and Zn) (not shown). Other lithophile elements positively correlated to Al and Fe, such as Mn and Ba, presented similar values to those reported for mosses from volcanic areas at northern Victoria Land, eastern Antarctica (Bargagli et al., 1998).

Mosses provide an effective morphology for entrapment of airborne particles (Bargagli et al., 1995; Bargagli, 1995) and normally grow at lowered areas where particle deposition is likely. At remote barren areas airborne particles are composed mainly by soil dust rather than anthropogenic emissions (Bargagli, 1995). Therefore, the levels of elements in mosses from areas such as Antarctica are intimately related to the biogeochemical nature of the environment (Bargagli et al., 1995). It is also known that the background concentrations of several elements increase proportionally to Al or Fe, independently of moss specie or analytical method (Bargagli et al., 1995).

The effect of substrate geochemistry in the total element levels in mosses is evident (Table 3). Consistently, Al and Fe are significantly higher for mosses collected on acid sulphate soils while Ca levels are significantly lower. These substrates were acidified by sulphides oxidation, with formation of amorphous Fe minerals and crystalline K/Fe-sulphates (Chapter 3). In these acid pedoenvironments, Ca-carbonate dissolution is favored with leaching of dissolved products whereas aluminum activity is increased (Chapters 2 and 3). The widespread mineralization of Cu-rich pyrite (FeS_2) in the hosting andesite accounts for high total Fe levels in soils (Albuquerque-Filho, 2005). High amounts of amorphous Fe minerals (Chapter 3) increase the bioavailability of this metal. Therefore, although contamination by soil particles may account for the higher Al and Fe values in mosses, an increase in plant uptake of these acid-soluble metals is also a possible explanation. Since these organisms grow on water logged areas, their elemental composition is greatly influenced by melting water chemistry which in its turn reflects the geochemistry of the areas drained by the water channels.

A significant increase of total P and Zn levels for mosses occurs due to ornithogenic influence. Significant positive relationships between soil P extracted with Melich-1 and the total levels of P, Ti, Cu, Ni and Zn suggest that guano deposition somehow increases bioaccumulation of these elements. This is probably due to the acidolysis caused by guano microbial mineralization (Tatur, 1989) which favors chemical weathering and increases the solubility of these lithophile elements.

Cd, Cr, and Pb were detected only in mosses that suffered some degree of ornithogenic influence. The levels obtained for these elements fall at the lower extreme of the concentration ranges reported for mosses growing in Antarctica (Bargagli et al.,1995; Bargagli, 1995) and other remote areas in both hemispheres (Bargagli et al. 1998), indicating low anthropogenic influence. Bargagli et al. (1998) also observed Cd enrichment in mosses growing close to penguin rookeries at Edmonson Point, east Antarctica and attributed this to sea-land transference via guano deposition. High bioavailability of Cd in Antarctic sea waters leads to bioaccumulation by crustaceous and fishes (Bargagli et al., 1996) which may explain the high Cd levels in guano (Bargagli et al., 1998). The transformation of guano deposits permits the transference of Cd to the terrestrial biota characterizing ornithogenic sites as important areas for monitoring heavy metal transference in Antarctic food webs.

Table 2 – Mean values, standard deviations (S.D.) and variation coefficients (V.C.) of macro and microelements in lichens, mosses and flowering plants from ice-free areas of Admiralty Bay, maritime Antarctica.

Vegetation	Al	Fé	Ca	Mg	K	P	Ti	Mn	Cu	B	Ba	Sr	Ni	Cd	Cr	Pb	V	Zn
	%						μg/g											
Mosses																		
Mean (n = 63)	1.26	1.58	0.75	0.57	0.33	0.22	331.6	301.4	58.1	67.3	38.3	53.5	7.7	0.1	0.05	0.07	52.2	43.7
S.D. (±)	0.80	0.99	0.35	0.25	0.17	0.15	288.1	184.9	33.6	64.4	57.1	51.7	8.4	0.1	0.27	0.26	29.62	22.20
V.C. (%)	*63.2*	*62.2*	*47.0*	*44.3*	*51.9*	*68.9*	*86.9*	*61.3*	*57.8*	*95.6*	*149.3*	*96.7*	*109.0*	*220.0*	*548.0*	*372*	*56.7*	*50.8*
Sanionia sp .(n= 50)	1.29	1.61	0.75	0.59	0.34	0.25	337.5	296.7	58.1	64.7	35.9	50.2	7.2	0.07	0.07	0.08	52.1	44.2
Polytrichum sp .(n=13)	1.22	1.53	0.75	0.55	0.31	0.13	318.3	325.8	59.8	81.4	43.1	68.9	10.2	n.d.	n.d.	n.d.	54.1	43.5
Epilithic lichens																		
Mean (n= 46)	0.07	0.09	0.87	0.05	0.12	0.05	25.2	10.1	9.1	28.6	n.d	34.8	4.9	0.1	0.5	0.4	8.6	8.4
S.D. (±)	0.05	0.07	0.72	0.04	0.05	0.02	28.4	12.3	13.0	5.1	0.0	16.2	6.1	0.2	0.8	0.8	11.8	9.7
V.C. (%)	*77.5*	*76.9*	*82.8*	*77.1*	*41.9*	*44.9*	*112.7*	*121.7*	*142.7*	*17.9*	-	*46.6*	*125.1*	*193.4*	*174.0*	*219.5*	*137.1*	*115.9*
Usnea sp.(n= 44)	0.07	0.09	0.91	0.05	0.12	0.05	27.2	10.6	9.3	28.6	n.d	34.8	4.9	0.1	0.5	0.4	8.8	8.5
S. globosus (n= 2)	0.07	0.10	0.08	0.13	0.13	0.06	2.0	n.d.	4.7	n.d	n.d	n.d	n.d	n.d	n.d	n.d	3.1	6.4
Flowering plants																		
Mean (n= 34)	0.78	0.78	0.51	0.45	0.42	0.23	184.2	274.0	43.0	72.9	16.9	65.0	6.7	0.1	0.1	0.1	30.5	42.9
S.D. (±)	0.52	0.50	0.21	0.18	0.27	0.10	150.7	143.9	32.2	31.4	36.7	24.3	7.9	0.2	0.2	0.2	19.4	19.6
V.C. (%)	*66.7*	*63.8*	*41.6*	*39.3*	*63.1*	*42.9*	*81.8*	*52.5*	*74.9*	*43.0*	*217.0*	*37.3*	*116.9*	*200*	*229*	*196*	*138.0*	*377.2*
D.antarctica (n = 20)	0.77	0.80	0.52	0.43	0.32	0.21	207.0	265.9	45.6	75.6	11.1	62.3	7.5	0.1	n.d.	0.08.	31.3	42.8
C. quitensis (n = 14)	0.80	0.73	0.48	0.50	0.65	0.26	132.0	293.3	36.9	38.3	30.1	99.6	2.7	0.4	0.1	0.4	28.6	43.1

Table 3 – Mean and variation coefficients (V.C.) of macro and microelements in mosses growing on different substrates.

Substrate	Al	Fe	Ca	Mg	K	P	Ti	Mn	Cu	Sr	Ni	Cd	Cr	Pb	V	Zn
	%						µg/g									
Acid sulphate soil	2.78	3.59	0.36	0.61	0.30	0.12	223.5	310.8	70.1	65.3	n.d.	n.d.	n.d.	n.d.	59.7	37.8
V.C. (%) n = 4	*27.2*	*26.5*	*35.9*	*26.6*	*51.5*	*31.0*	*138.1*	*29.3*	*59.11*	*54.18*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*25.2*	*13.1*
Basalt/andesite	1.2	1.6	0.9	0.6	0.3	0.2	300.7	361.2	50.1	67.1	7.1	n.d.	n.d.	n.d.	44.6	42.0
V.C. (%) n = 28	*59.1*	*60.3*	*48.4*	*42.9*	*42.2*	*62.4*	*93.3*	*66.5*	*64.2*	*77.0*	*135.4*	*n.d.*	*n.d.*	*n.d.*	*74.4*	*62.8*
Ornithogenic sites	1.0	1.32	0.72	0.52	0.39	0.32	398.4	249.7	64.5	41.5	9.5	0.12	0.12	0.13	58.84	46.68
V.C (%) n = 31	*58.5*	*53.5*	*37.5*	*47.6*	*56.7*	*54.2*	*77.7*	*46.6*	*53.0*	*128.6*	*79.3*	*149.8*	*377.1*	*279.6*	*46.1*	*42.3*

Table 4 – Mean and variation coefficients (V.C.) of macro and microelements in *Deschampsia antarctica* growing on different substrates[1] at both western and eastern coasts of Admiralty Bay

Substrate	Al	Fe	Ca	Mg	K	P	Ti	Mn	Cu	Sr	Ni	Cd	Cr	Pb	V	Zn
	%						µg/g									
Acid sulphate soil	0.90	1.36	0.47	0.39	0.44	0.20	113.9	306.3	41.6	42.11	n.d.	n.d.	n.d.	n.d.	11.7	31.1
V.C. (%) (n = 3)	*61.4*	*66.6*	*24.8*	*45.0*	*48.5*	*35.8*	*89.9*	*51.1*	*88.1*	*45.60*	*n.d.*	*n.d.*	*n.d.*	*n.d.*	*133.6*	*66.9*
Basalt/andesite. - West coast	0.74	0.74	0.49	0.43	0.21	0.19	281.3	211.0	41.3	71.2	8.5	0.18	0.06	0.1	37.6	41.6
V.C. (%) (n = 10)	*81.0*	*62.7*	*43.0*	*48.3*	*95.3*	*55.4*	*39.6*	*39.2*	*66.3*	*36.5*	*93.8*	*104.8*	*318.0*	*188.9*	*54.3*	*48.3*
Basalt/andesite. - other	0.83	0.74	0.56	0.51	0.51	0.24	154.0	369.9	48.7	65.3	2.7	n.d.	n.d.	n.d.	25.6	49.3
V.C (%) (n = 7)	*58.9*	*42.8*	*42.4*	*20.6*	*48.3*	*39.2*	*107.2*	*46.0*	*82.2*	*33.2*	*223.6*	*n.d.*	*n.d.*	*n.d.*	*61.5*	*36.8*

[1] all sites with *Deschampsia* have some degree of ornithogenic influence

3.2 Lichens

Lichens are recognized worldwide as good bioindicators of atmospherically-transported heavy metals. Due to the lack of cuticle and stomata, all nutrients including trace metals are incorporated from the atmosphere (Conti and Cecchetti, 2001). In Antarctica, *Usnea* species are widespread and survive even in the most severe conditions. Poblet et al. (1997) have proposed the choice of *Usnea Antarctica* and *U. aurantiacoatra (Usenea sp.)* as biomonitors of heavy metal distribution in Antarctica. However, very few data is available on the concentration of different elements for these organisms (Poblet et al., 1997; Bargagli and Focardi, 1992).

The total levels of all elements except for Ca were extremely lower than those obtained for mosses and flowering plants (Table 2). The mean Fe level obtained for *Usnea sp* from Admiralty Bay was slightly higher than that reported for the same species from other parts of King George Island (Poblet et al., 1997). The extremely high Ca/Al and Ca/Fe ratios (not shown) suggest that Ca is very important for the development of *Usnea* species. On the other hand, for *Sphaerophilous globosus,* Ca levels were ten times lower but Al and Fe were comparable to those obtained for *Usnea sp*.

In the present study, Cd, Pb and Cr levels were higher in *Usnea sp.* than in any other organism. The levels obtained are lower than that reported for several lichen species from different parts of the world (Conti and Ceccheti, 2001). In terms of Antarctic ecosystems the value obtained for Cd (0.1 µg/g) is higher than that presented by Poblet et al. (1997) for *Usnea sp.* from King George Island (0.008 ± 0.015 µg/g) but similar to those reported by Bargagli and Focardi (1992) for *Usnea antarctica* from eastern Antarctica (0.16 ± 0.09 µg/g). The range of Pb level (0.4-3.74 µg/g) is within the range reported by previous works for *Usnea sp.* in Antarctica (0.95 - 4.76 µg/g, Poblet et al., 1997; Bargagli and Focardi (1992). These results indicate low anthropogenic impact and may be used for environmental monitoring and future studies. Despite the extremely low values, we found higher bioaccumulation of Cd, Cr and Pb in organisms colonizing the western coast of Admiralty Bay, which is the oldest ice-free area.

3.3 Flowering plants

Deschampsia antarctica and *Colobanthus quitensis* are the only two higher plants growing in Antarctica and are restricted to maritime Antarctica. All sites where these plants occur have some degree of ornithogenic influence. The soils are acidic, with relatively high organic matter and P levels (Tatur et al., 1997; Michel et al, 2006; Chapter 2). The presence of a proper root system results in completely different absorption mechanisms than cryptogamic organisms. We found only one reference on elemental levels for *D. antarctica* (Tatur et al., 1997) and none regarding *C. quitensis.*

Our data suggests that both plants accumulate similar amounts of all elements studied, except for K, Cd and Pb, which were significantly higher for *Colobanthus quitensis* (Table 3). Total Ca, Fe, Mn, Cu and Sr values for *D. antarctica* were higher than those reported by Tatur et al., (1997) and the levels of P, Mg and K were lower. The total Zn level and Ca/Mg ratio were similar to that reported previously for *D. antarctica* (Tatur et al., 1997).

D. antantartica colonizing acid sulphate soils presented significantly higher Fe and lower Mg levels when compared to plants growing on basaltic/andesitic substrates evidencing that parent material geochemistry alters metal bioaccumulation. The Cd level was significantly higher for *D. antarctica* from the western coast of Admiralty Bay (data not presented), corroborating the idea of sea-land transference of heavy metals via guano deposition, mainly by penguins. We have found no references in the literature to the levels of Cd, Cr, Pb, Ni in *Deschampsia antarctica*.

4. Conclusions

The low levels of Cd, As, Cr, Ni, Pb for all studied organisms in relation to other remote areas suggest negligible contamination by anthropogenic emissions in vegetation communites of Admiralty Bay. The highest levels of Cr, Cd and Pb for *Usnea* species indicate that these elements are mainly related to airborne particles rather than to the geological substrate and support the use of epilithic lichens as efficient biomonitors of anthropogenic impacts in Antarctic terrestrial ecosystems.

Our results confirm previous works and indicate that bioaccumulation of metals in mosses and *D. antarctica* from Antarctica is greatly determined by substrate geochemistry. Higher Cd levels in *Deschampsia* a*ntarctica* and mosses with increasing ornithogenic influence suggest that these sites may be useful for monitoring heavy metal sea-land transference along Antarctic food webs.

Due to the highly variable levels for all elements and all organisms studied, it is necessary to establish permanent monitoring sites to be sampled periodically in order to avoid site-specific variations which may lead to misinterpretations and inadequate comparisons of element levels in future monitoring schemes.

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CONCLUSÕES GERAIS

Os solos da Baía do Almirantado podem ser agrupados em: solos basálticos/andesíticos, solos tiomórficos e solos ornitogênicos. O primeiro grupo ocupa a maior parte das áreas livres de gelo enquanto os dois últimos são restritos a áreas com veios de andesito piritizado (solos tiomórficos) e colônias de aves (solos ornitogênicos). Devido à presença de *permafrost* os solos são classificados como *Gelisols* ou *Cryosols* de acordo com o sistema americano ou da FAO, respectivamente.

Em geral são solos pouco desenvolvidos com características morfológicas, mineralógicas, químicas e físicas estreitamente relacionadas ao material de origem. Nos solos basálticos a fração argila é formada através do intemperismo físico com presença de piroxênio e feldspato no tamanho argila. Ocorre o intemperismo químico incipiente com formação de esmectitas com hidroxi-Al entre camadas e formas pouco cristalinas de Al e Si (alofana).

Nos solos tiomórficos, ocorre formação de jarosita e ferridrita através da oxidação da pirita, resultando em elevada acidez e intenso intemperismo químico. A interação entre o guano das aves e o substrato mineral em áreas de nidificação de pingüins resulta na formação de fosfatos cristalinos e amorfos que controlam as características químicas dos solos ornitogênicos. As áreas adjacentes às colônias de pingüins são afetadas por lixiviados ricos em P, com formação apenas de fosfatos amorfos.

Do ponto de vista micromorfológico os solos apresentam feições típicas de solos de áreas polares, nos quais o congelamento e descongelamento originam microestruturas granulares altamente estáveis em solos com maior teor de silte e argila. Análises microquímicas permitiram o estudo sub-microscópico e o detalhamento dos processos de formação de jarosita e de fosfatização. Ao contrário dos solos da antártica continental, o intemperismo químico é um processo ativo nos solos da Baía do Almirantado, com dissolução de alumino-silicatos primários e lixiviação limitada do Al, Fe e Si dissolvidos. Em algumas áreas o intemperismo químico é acelerado em função da oxidação de sulfetos e em outras pela atividade da avifauna.

A atividade de aves resulta no desenvolvimento de extensas coberturas vegetais com a presença das duas únicas plantas superiores que crescem na Antártica (*Deschampsia antarctica* Desv. (Poaceae) and *Colobanthus quitensis* (Kunth) Bartl. (Caryophyllaceae)). Estas áreas apresentam os maiores estoques de C orgânico no solo, com formação de horizontes hísticos fibrosos. Solos mais desenvolvidos apresentam maior participação das frações ácido fúlvico e húmico.

Os níveis de metais pesados em todas as espécies vegetais estudadas foram muito baixos, indicando praticamente nenhum efeito de contaminação antrópica. Os teores de elementos em musgos e plantas superiores refletem a geoquímica do material de origem enquanto em liquens epilíticos do gênero *Usnea* os níveis de elementos estão relacionados a particulados atmosféricos. Parcelas permanentes devem ser implantadas para o monitoramento dos teores de elementos em plantas de forma e minimizar a variação em função da natureza geoquímica do substrato.

O presente trabalho permitiu conhecer melhor os ecossistemas terrestres da Baía do Almirantado e os processos pedogenéticos. Percebe-se, no entanto, que ainda existem muitas lacunas a serem preenchidas. Neste sentido, pesquisas voltadas para o monitoramento da dinâmica do *Permafrost*, o estudo do aumento das áreas livres de gelo e estudos sobre os processos de transformação dos materiais orgânicos na Antártica são necessárias.