A Case for Chemical Weathering in Soils of Hurd Peninsula, Livingston Island, South Shetland Islands, Antarctica

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Abstract

The soils of the South Shetland Islands, Antarctica are considered weakly developed. Chemical weathering processes are generally considered to be negligible except in areas that receive large additions of seabird guano. In this paper we describe and analyze 19 soils on Hurd Peninsula, Livingston Island in the South Shetland Island Archipelago. The soils were classified according to US Soil Taxonomy and were generally weakly developed Gelorthents, Humigelepts and Haploorthels. However, B horizon formation, rubification and increases in extractable iron and aluminum were observed on toposequences of raised beaches. The deposition of tephra and/or guano are likely responsible for the chemically driven processes. Guano deposits contain phosphates and oxalic acid, causing phosphatization and/or dissolution of silicates. Input of tephra with easily weatherable minerals may account for metastable mineral formation. Tephra deposition in the oldest raised beaches has formed a fine-textured mantle overlying the coarser textured subsoils. Highly weatherable tephra, as opposed to guano deposition, appears to influence soil formation at Hurd Peninsula.

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25 **Key words:** Antarctic Soils, Entisols, Tephra, Ornithogenic Soils, Soil Weathering

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Introduction

The main processes driving soil formation in the South Shetland Islands have been cited as ornithogenic and physical or mechanical weathering (Simas *et al.*, 2008). The literature bears little support for chemical weathering as an important soil forming process in maritime Antarctica. Ornithogenic soils (i.e. soils with properties produced by avian activities) have been described in several locations in the South Shetland Islands, on the Antarctic Peninsula, and at several maritime locations along continental Antarctica (Michel *et al.*, 2006; Simas *et al.*, 2006; Simas *et al.*, 2007; Tatur, 2002). Phosphatization is an ornithogenic soil forming process that produces a unique suite of phosphate minerals that is indicative of zones of active or relict manuring by seabirds (mainly penguins). Phosphatization occurs when phosphorus rich guano, mostly from penguins, interacts with water and soils. Fresh guano has a neutral pH and initial stages of degradation enrich the surface of penguin rookeries with urates, ammonium, chitin, struvite ($[\text{NH}_4]\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) and apatite ($\text{Ca}_5[\text{PO}_4]_3[\text{OH}, \text{F}, \text{Cl}]$) (Myrcha and Tatur, 1991). Volatilization and nitrification of ammonium ions and various hydrolysis reactions cause phosphorus laden acidic solutions to percolate downwards, causing the following set of phosphate minerals to precipitate: leucophosphite ($\text{KFe}^{3+}_2[\text{PO}_4]_2[\text{OH}] \cdot 2\text{H}_2\text{O}$); minyulite ($\text{KAl}_2[\text{PO}_4]_2[\text{OH}]_{0.75}\text{F}_{0.25} \cdot 4\text{H}_2\text{O}$); metavariscite ($\text{Al}[\text{PO}_4] \cdot 2\text{H}_2\text{O}$); vashegyite ($\text{Al}_6[\text{PO}_4]_5[\text{OH}]_3 \cdot 22\text{H}_2\text{O}$); arctowskite ($\text{Al}_9[\text{PO}_4]_8[\text{OH}]_3 \cdot 27\text{H}_2\text{O}$); and vivanite ($\text{Fe}^{2+}_3[\text{PO}_4]_2 \cdot 8\text{H}_2\text{O}$) (Myrcha and Tatur, 1991; Pietr *et al.*, 1983; Simas *et al.*, 2007; Tatur, 1989). The unique chemistry of ornithogenic soils and the identification of phosphate minerals in abandoned rookeries hundreds of years old have prompted several researchers to suggest "Ornithogenic" as an additional subgroup to Soil *Taxonomy* (Michel *et al.*, 2006; Simas *et al.*, 2007).

Soils at Hurd Peninsula, Livingston Island, in the South Shetland Island Archipelago, are not only impacted by ornithogenic activity, but also receive some of the highest levels of tephra deposition from volcanic activity at nearby Deception Island (Baker *et al.*, 1975; Lee *et al.*, 2007). Tephra is a pyroclastic material dominated by amorphous glass-like materials that weather to produce Al and Si rich minerals. The majority of tephra is andesitic origin and weathers to produce an acidic environment favoring the formation of allophane and Al-organic matter complexes typical of Andisols (Schaetzl and Anderson, 2005).

Previous soil investigations at Hurd Peninsula have been conducted by Moura *et al.* (2012), Ganzert *et al.* (2011), and Navas *et al.* (2008). Navas *et al.* (2008) described and analyzed the chemical properties, physical properties, and mineralogy of 7 profiles from nearby Byers Peninsula, the largest ice-free area in South Shetland Islands at 60 km²) and 4 profiles from Hurd Peninsula to determine how soil properties varied with lithology. The study concluded that bedrock lithology was more correlated with soil properties than physiographic location or geomorphic unit and that physical weathering by freeze-thaw processes, as opposed to chemical weathering, controlled soil formation. The goal of this study is to study soil-forming processes on Hurd Peninsula, particularly in response to guano deposition from nearby penguin colonies and volcanic ash deposition from the nearby Deception Island. Understanding how penguin guano deposition is important because the alterations to the soil by guano mineralization have several unique and poorly understood effects. Similarly, the mineral and nutrient contributions from the weathering of volcanic ash on soils are virtually unknown in polar regions, such as the Antarctic Peninsula.

Materials and Methods

Study Area

Hurd Peninsula, Livingston Island (62°39'S) is a 20 km², north facing bedrock upland with a maximum elevation of 400 m (Fig. 1). The peninsula receives approximately 800 mm of precipitation per year and has a mean air average temperature (MAAT) between -1.5 to -3.2°C at 15 m above sea level (a.s.l.), and approximately -4.5 °C at 275 m a.s.l. (recorded between 2000-2006), with a range of 10°C to -35°C (Ganzert *et al.*, 2011; Hauck *et al.*, 2007; Moura *et al.*, 2012). Air temperatures are generally positive from December to March and negative from April through November, with very high humidities (80-90%) encountered during the summer months due to the influence of the polar front (Hauck *et al.*, 2007).

Hurd Peninsula is comprised of Mesozoic sedimentary rocks of the Miers Bluff Formation, which are mainly shales, siltstones, arkosic greywackes, and sandstones with some interbedded conglomerates derived from volcanics and erosion of a volcanic island arc, subsequently deposited as deep-water turbidites (Hobbs, 1968). The ice-free areas of Hurd Peninsula are located along the coast while the center of the peninsula is covered by an ice dome rising to 330 m a.s.l. The southern part of Hurd Peninsula is a rugged ice-free coast bordering False Bay that has a maximum elevation of 400 m a.s.l. and terminates as coastal cliffs or very steep bedrock slopes. The northerly side along South Bay has a more gentle topography with a maximum height of 275 m a.s.l. and a marine eroded platform between 60 to 200 m a.s.l. that is bisected by sloping glacially cut valleys filled with raised marine beaches.

The raised beaches on Hurd Peninsula have been classified as 1) lower beaches (1-3 terraces) under 2 m a.s.l. to the modern beach that have clean pebbles without lichens; 2) intermediate beaches (4-8 terraces) between 2.8 and 8 m a.s.l. with lichens; and 3) upper beaches (1-4 terraces) between 12 and 18.6 m with lichens and *Deschampsia antarctica* (Lopez-Martinez

100 *et al.*, 1992). The radiocarbon dates of raised beaches at nearby Byers Peninsula suggests the
101 lower beaches formed less than 200 years BP; the intermediate beaches formed about 200 to
102 2000 years BP; while the upper beaches formed between 2000 to 6000 years BP (Clapperton and
103 Sugden, 1988).

104 Above the raised beaches are early Pliocene to late Miocene marine eroded platforms 60-
105 200 m a.s.l. which are mostly sediment-free with the exception of a veneer of frost shattered
106 materials and the occasional rounded stone (Pallás *et al.*, 1995). Regional tectonic uplift is likely
107 responsible for the marine eroded platforms which bear evidence of faulting, while the raised
108 beaches which show no evidence of fault deformation are likely the result of isostatic and
109 glacioeustatic changes. Geomorphic descriptions and maps of Hurd Peninsula can be found in
110 Lopez-Martinez *et al.* (1992) and Pallás *et al.* (1995).

111 Following the last glacial maximum, the ice sheet had retreated to at least the location of
112 the upper raised beaches by 6000 BP, but readvanced at least twice between 720-330 BP and
113 after 300 BP), depositing occasional recent moraines over raised beaches (Pallás *et al.*, 1995).
114 The unconsolidated sediments that make up the soils on the peninsula include marine alluvium
115 on the raised beaches and glacial tills at Bulgarian Bay. Both sources are intermixed with frost
116 shattered rock of the Miers Bluff formation and volcanic ash derived from eruptions of nearby
117 Deception Island. Hurd Peninsula is particularly prone to tephra deposition from pyroclastic
118 eruptions of Deception Island volcanism, as shown by isopachs of a 1970 pyroclastic eruption of
119 Deception Island (Baker *et al.*, 1975).

120 At least five known tephra layers, ranging in thickness from a few millimeters to 0.03 m,
121 crop out of ice cliffs on the site. These five layers are correlated to pyroclastic eruptions that took
122 place between the early 19th century and today (Pallás *et al.*, 2001). In short, there is physical

heterogeneity in soils across the peninsula, while the chemistry is relatively consistent and dominantly a basaltic andesite composition (Baker *et al.*, 1975).

Periglacial features are commonly found on the glacial till and include patterned ground, rock glaciers, and stone banked lobes (i.e. sloping solifluction terraces). Permafrost is found continuously above 30 m a.s.l., with active layer thicknesses decreasing with elevation; Mt. Reina Sofia (275 m a.s.l.) has an active layer thickness less than 1 m deep (Hauck *et al.*, 2007). Cryoturbation features observed in soils by Navas *et al.* (2008) indicate that periglacial conditions were more extensive in the recent past.

Metcheva and Zehtindjiev (2005) estimated the abundance of birds at Hurd Peninsula in 2004 and found 90 nests of *Pygoscelis papua* (Gentoo Penguin) at Caleta Argentina (cove to the west of Spanish Cove), 3,600 nests of *P. antarctica* (Chinstrap Penguin) at Miers Bluff and 30 nests of *P. papua* at Caleta Buena Nueva on the southern coast along False Bay. Occasional occupation of penguins on the raised beaches is evidenced by common penguin excreta on several of the current and raised beaches. *Stercorarius antarcticus* (Brown skua) is common in areas adjacent to penguin colonies, especially above the large colony at Cape Hurd where they are found in abundance.

The vegetation of Hurd Peninsula consists of lichens (mainly species of *Himantormia*, *Usnea* and *Umbilicaria*), mosses (mainly *Andreaea*-rock moss and *Drepanocladus*-carpet moss) and *Deschampsia antarctica* (Antarctic hair grass). Associations of rock mosses and lichens are commonly encountered and can be found covering up to 90% of the oldest ice-free surfaces at all elevations. Carpet mosses and *D. antarctica* occur both at lower elevations and on the raised beaches; typical surface coverage on the raised beaches is 1-30% (and up to 50%). Algal mats of *Prasiola crispa* that are commonly encountered near rookeries in the South Shetlands are rarely

found at Hurd Peninsula.

Soil Sampling

A total of 19 soils were excavated to depths of up to 75 cm and 64 samples were collected during the austral summer of 2011. Soils were collected from the following areas: Bulgarian Bay, Spanish Cove, Miers Bluff and Mt. Riena Sophia. The pedon locations were selected to represent the different geomorphic surfaces that occur on Hurd Peninsula as well as to evaluate soil characteristics of a sequence of raised beaches. This is a judgment-based sampling strategy typically used to collect observational data for soil landscapes where little previous research has been conducted (Dijkerman, 1974). The soils were examined by hand-dug pits and described according to *Soil Taxonomy* (Soil Survey Staff, 2010). The symbol “D” was used to describe surface stone layers. Frozen soil materials are identified by the subscript “f” which if described late in the Antarctic summer is likely synonymous with permanently frozen ground. Site and soil classifications schemes (e.g. soil depth class) were determined according to the *Soil Survey Manual* (Soil Survey Staff, 1993).

Soil Analysis

All soil samples were air dried prior to shipment to the laboratory for further analyses. The soil samples were shipped to the laboratory in plastic bags. Upon arrival the soils were passed through a 2 mm sieve, and the percentage of coarse fragments >2 mm was recorded. Soil pH was performed on a 1:1 soil to distilled water solution and a 1:2 soil to 0.01M CaCl₂ solution; and electrical conductivity from a 1:2 soil to distilled water solution. Carbonates have been shown to be almost entirely absent from the soils of Hurd Peninsula (Navas *et al.*, 2008); their presence

was tested by application of dilute 1M HCL acid to air-dried soils. Particle size distribution was determined by laser-light diffraction on a Coulter LS230 laser according to the method of Arriaga *et al.* (2006). Total carbon and nitrogen were tested by combustion on a Flash EA 1112 16 CN Automatic Elemental Analyzer (Thermo Finnigan, Milan, Italy). Soils with a non-effervescent reaction class were assumed to have total carbon approximately equal to organic carbon. Total phosphorus, potassium, calcium, magnesium, iron, aluminum, and sodium were determined by microwave digestion with HCl and H₂SO₄ and detection by ICP-OES (Maguire and Heckendorn, 2011). Total iron-oxides were determined by dithionite-citrate extraction according to the method of Holmgren (1967) with detection by ICP-OES.

In order to determine the presence of tephra in Hurd Peninsula soils, 10 fine grained samples were examined using electron beam microscopy and microanalytical techniques with the University of Wisconsin-Madison Department of Geoscience's Hitachi S3400 scanning electron microscope (SEM) and CAMECA SX-51 electron probe microanalyzer (EPMA). Samples were cast in epoxy in one-inch diameter rings, wet polished using progressively finer SiC papers, with a final 0.35 micron diamond polish. They were then coated with ~200Å of carbon to allow high vacuum (no charging) in the SEM and EPMA.

The electron beam instruments provided three techniques: backscatter electron (BSE) imaging, semi-quantitative energy dispersive spectroscopy (EDS), and quantitative, standards-based wavelength dispersive spectroscopy (WDS). Similarly, six soil samples from the nearby Deception Island, which contains an active volcano, were also examined for possible source matches. These techniques examined soil samples for the presence of volcanic glass containing crystals and vesicles that are generally associated with volcanic ash (Fisher and Schmincke, 1984). Once the presence of tephra was confirmed using SEM and BSE imaging assisted by

EDS, and target grains chosen, the exact chemical composition of the glass in the identified tephra was determined by EPMA-WDS. These glass compositions – both the Herd Peninsula and the Deception Island ones -- can then be compared to published analyses of volcanic glass sampled throughout the Antarctic (Kraus *et al.*, 2012).

Results

Pedon Properties

Soils on Spanish Cove classify as Gelorthents at the lower elevations (< 8 m a.s.l.) and Humigelepts at higher elevations (12-28 m a.s.l.). The pedons at Spanish Cove formed on a toposequence of raised beaches with little periglacial alteration. Raised beaches were excavated on terraces 4, 5, 6, 8, 12, 13, 18, and 28 m a.s.l. (Table 1). For the purposes of this paper the 4-8 m raised beaches will be considered Lower Spanish Cove (LSC) and 12-28 m, Upper Spanish Cove (USC). The soils on the raised beaches formed in rounded to subrounded marine sediments intermixed with volcanic tephra. The 28 m raised beach is above the maximum elevation of contemporary raised beaches described in the literature for the South Shetland Islands. It is unclear if these are indeed contemporary raised beaches or represent one of the older marine platforms that have been described on Livingston Island attaining heights of 143 m (John and Sugden, 1971). The 4, 5, and 6 m raised beaches were the only ones to have a significant accumulation of vegetation; the 4 m raised beach was dominated by nearly 50% *D. antarctica* while the 5 and 6 m raised beaches were dominated by lichens. Coincidentally, the 4, 5, and 6 m raised beaches were also the only with visible penguin excreta deposits on the surface. A scattering (< 5%) of mosses appeared on the 12 m and higher raised beaches. The pedon described at Mt. Reina Sophia (L19) was a Typic Haploturbel that formed in mixed till and frost-

shattered rock that has formed non-sorted circles. Permafrost was detected between 0.9 m and 1.0 m (Hauck *et al.*, 2007), supporting classification as Gelisol.

The pedons above Bulgarian Beach (BB) formed in till intermixed with frost-shattered rock and tephra. The geomorphic features ranged from glacial to periglacial; raised beaches do not occur in this area. The formation of stone-banked lobes is very common in the area. Vegetation is sporadic with pockets of dense lichen or moss cover in an otherwise unvegetated landscape. Bird activity is low presumably due to the lack of easy shore access in the absence of raised beaches.

The Miers Bluff (MB) pedons formed on raised beaches that are also slightly above the maximum elevation of raised beaches previously described in the South Shetland Islands. The site is immediately adjacent to a > 200 m long rock glacier. The site has several nesting pairs of Skuas that prey on a large chinstrap penguin rookery (>3,000 nests) located on the current beach below. An association of *D. antarctica*, lichens and mosses covers up to 15% of the ground surface.

Presence of Tephra

The demonstrated presence of tephra in soils of Hurd Peninsula indicates the contribution of volcanic ash on soil development on Livingston Island. Vesicular volcanic glass associated with gas-rich magma eruptions and aerial dispersal was found to be common in the soils of the Hurd Peninsula (Fig. 2). Within the volcanic glass were vesicles created when dissolved gasses exsolved due to the pressure drop during eruption. In association with the vesicles were FeTi-oxide crystals which nucleated during eruption and were frozen together when the glass was quenched. Most tephra samples were basaltic to andesitic in composition (SiO_2 ~50-54%),

which is a composition strikingly similar to the tephra analyzed from Deception Island. A point count of volcanic fragments (based on presence of vesicles or glassy texture) conducted on 400 Hurd Peninsula samples determined that 73-92% of the fragments had extrusive volcanic origins.

Using EPMA we examined the glass in 43 tephra fragments from Hurd Peninsula and 15 fragments from Deception Island to determine the major and minor element oxides present in the soil samples. Oxides examined included SiO₂, Na₂O, MgO, Al₂O₃, P₂O₆, K₂O, CaO, FeO, MnO and TiO₂. SiO₂ was used as the common comparison variable (Lowe *et al.*, 2014) (Fig. 3). There was a good correlation for several oxides, especially MgO, K₂O and CaO, and many outlier samples found on Hurd Peninsula were also detected from Deception Island samples.

Soil Properties

Mean, median and standard deviation of the major soil nutrients for all the sites examined at Hurd Peninsula were: total-carbon (0.451%, 0.303%, 0.446); total-nitrogen (0.080%, 0.063%, 0.046); and total-phosphorus (0.178%, 0.046%, 0.046) (Table 2). The average pH and EC were 6.6 (range of 4.6-8.2) and 29.3 mS m⁻¹ (range of 10-115). The textures were mainly coarse sands with average sand, silt, and clay quantities of 82.9%, 11.6%, and 5.6%, respectively, while the > 2 mm coarse fragments averaged 49.1%.

The toposequence of raised beaches at Spanish Cove show differentiation with increasing elevation. Rubification and horizonation of the Upper Spanish Cove (USC) raised beaches increases with elevation (L09, L16, L17 and L18) starting at the 12 m a.s.l. (Fig. 4). Paralleling these changes is the development of an approximately 0.3 m fine layered mantle overlying coarser materials. The Lower Spanish Cove (LSC) raised beaches (L05-08) lack the finer textured mantle and have significantly less silt and fine sand than the USC raised beaches (Table

3). Similar to the USC sites, the raised beaches at Miers Bluff (MB) also display increases in rubification, horizonation, and fine-textured material accumulations. In general, the LSC raised beaches were coarser in both the fine earth and coarse fragment fraction than the other soils.

Total carbon and nitrogen are similar for both the USC (0.84 and 0.12%, respectively) and MB (0.70 and 0.12%, respectively) raised beaches and are significantly higher than the LSC (0.22 and 0.05% respectively) raised beaches or the glacially derived Bulgarian Bay (BB) soils (0.16 and 0.05%, respectively). Total-phosphorus on the MB soils were an order of magnitude greater than total-phosphorus measured on the USC soils. Total-P for the USC and LSC raised beaches and the glacial soils at BB were approximately 0.05% while the MB raised beaches averaged nearly 1%. Total-phosphorus was greater than 1% in the lower horizons of L10 (23 m MB raised beach) and reached 2.68% in the BC horizon of L12 (26 m MB raised beach). Total-calcium increased in L10 from 0.36% in the A horizon to 0.76% in the 2Bw and then decreased to approximately 0.20% in the lowest horizons. In the BC horizon of L12 total-calcium was 2.52%, a nearly stoichiometric increase with total-phosphorus in the same horizon which strongly indicates the presence of apatite minerals. Total-calcium between the BB soils and the USC soils was not significantly different, but total-calcium was significantly lower on the LSC soils. Total-magnesium was not significantly different among all sites, except the MB raised beaches where it was found at half the concentrations (Table 3). Total-potassium for MB on the other hand was found at concentrations more than two times higher than the other sites and reached 0.34% in the BC horizon of L12.

The rubification of the subsoils in the USC and MB raised beaches was accompanied by an approximately 30% increase in the (citrate-dithionite extracted) iron and 50% increase in (citrate-dithionite extracted) aluminum compared to the LSC raised beaches. In addition to a

general increase in total iron and aluminum for the USC and MB soils, a clear “bulge” in oxide-iron and -aluminum is also evident in the subsoils above the 12 m raised beach as shown in Fig. 5 for the Spanish Cove raised beaches. Data from the oxalate extraction (data not shown) gave statistically similar results to the citrate-dithionite extraction, presumably due to the non-crystalline nature of iron oxides in these soils (Schwertmann, 1973).

The pH values increased from 5.87 on the LSC raised beaches to 6.73 on the USC raised beaches. The glacial soils at BB were also significantly higher than the LSC soil while the MB raised beaches were slightly higher than the LSC raised beaches but not significantly so (Table 3).

Discussion

Previous researchers have stated that the major mechanism of weathering on the Antarctic Peninsula in the absence of birds is mechanical breakdown (Hauck *et al.*, 2008). However, the clear developmental age trends observed at the soils of Hurd Peninsula indicate that chemical weathering is occurring. In the oldest, most elevated raised beaches (USC and MB), the subsoil shows rubification and the formation of Bw horizons. In the USC and MB raised beaches, there is an increase in metals (total iron and aluminum), and in base cations (calcium, magnesium, and potassium), relative to both the younger raised beaches at LSC, and the glacially derived soils at BB (Table 3). In addition, the bulge in the data showing total oxide iron and aluminum extracted by citrate dithionite suggests translocation of iron and aluminum into the subsoil (Fig. 5).

Mechanisms of Chemical Weathering

Soils at Hurd Peninsula are subject to both tephra and guano deposition. Chemical weathering is

likely driven by these additions by one or a combination of the following mechanisms: (i) enhanced ion complexation in the presence of oxalic acid from uric acid decomposition, (ii) phosphate promoted dissolution, and (iii) rapid weathering of tephra.

(i) Oxalic acid promoted dissolution

Nearly 50% of bird excrement is composed of nitrogenous compounds (Pietr *et al.*, 1983), of which approximately 70% is uric acid (Hutchinson, 1950). Uric acid rapidly converts to oxalic acid or oxalate in terrestrial ecosystems (Lindeboom, 1984). Oxalate promotes dissolution of silicate minerals at oxalate solutions greater than 90 ppm (Barman *et al.*, 1992; Drever and Stillings, 1997; Stillings *et al.*, 1996). Typically, concentrations of oxalate in soils are less than 90 ppm; however Roser *et al.* (2004) observed oxalic acid concentrations in soils under an active penguin rookery soils at Windmill Islands, Antarctica, of more than 2,000 ppm oxalic acid. The low temperatures of Hurd Peninsula soils are unlikely to inhibit oxalate enhanced dissolution as oxalate has been shown to promote weathering in the extremely low temperatures of the Antarctic Dry Valleys (Johnston and Vestal, 1993). The mechanism behind enhanced oxalate dissolution is uncertain, specifically whether oxalic acid impacts dissolution through kinetic or thermodynamic affects. Oxalic acid may impact the kinetics of dissolution by complexation reactions that take place at the surface whereby oxalic acid binds directly with surface ions to promote dissolution. Oxalic acid may change mineral dynamics by lowering solution pH, thereby enabling proton-attack in low-pH conditions (< 4). Alternatively, oxalic acid may alter the stability of a mineral phase through complexation of ions in solution (particularly aluminum), acting to alter saturation state with respect to the primary phase, thereby enhancing dissolution relative to precipitation (Drever and Stillings, 1997). The older uplifted beaches (USC and MB)

have had a longer period of time to be nested by penguins, allowing for oxalic acids to interact with, dissolve and transport iron and aluminum in mineral soils.

(ii) Phosphate promoted dissolution

Crystalline phosphates are common to subsurface soils in Antarctica that have received heavy inputs of guano, exceeding total phosphorus levels of 4% under penguin rookeries. The dissolution of silicates and precipitation of minerals such as Palmerite ($\text{HK}_2\text{Al}_2(\text{PO}_4)_3 \cdot 7\text{H}_2\text{O}$) has been shown to occur under laboratory conditions (Haseman *et al.*, 1950). The experiments of Haseman *et al.* (1950) showed that dissolution of primary clay minerals in the presence of phosphate-solutions resulted in reprecipitation of phosphates in mineral phases such as Palmerite, Barrondite, Variscite, and Strengite with mobilization of iron and aluminum to the leachate. However, they found the rate of this process was only significant at temperatures exceeding 49° C and at pH conditions less than 5. Thus, the ability of phosphate to induce chemical weathering, although experimental possible, is unlikely in the climate and pH settings observed in Hurd Peninsula soils. Furthermore, while there is a significant increase in phosphorus in the soils found in the USC verses the LSC raised beaches, the increase barely exceeds the average abundance of phosphorus in the earth upper crust (Taylor and McLennan, 1995).

(iii) Rapid weathering of tephra

Tephra is added to the soils at Hurd Peninsula from nearby Deception Island, which erupts frequently enough that observable accumulations of sand-sized material occurs. Tephra from Deception Island is basaltic andesite and composed of scoriaceous glass and phenocrysts of

plagioclase microlites; detailed chemical composition of the tephra from Hurd Peninsula can be found in Pallás *et al.* (2001).

The glassy nature of tephra results in its rapid weathering in the soil environment with a half-life of less than 10,000 years (Dahlgren *et al.*, 1999). White (1983), observed that species such as sodium, potassium and aluminum within glassy tephra are easily diffused away from the glass surface and that it is likely that charge balance is maintained by the uptake of protons from solution thereby raising pH during dissolution of fresh tephra. Extremely high levels of extractable Al evident in the subsoils of the raised beaches above 12 m suggest that tephra dissolution and translocation of weathering products has occurred. To investigate if tephra deposition could possibly explain the high pH in the older and more developed soils, 10 grams of tephra (as measured by Pallas *et al.*, 2001) dissolved in 100 L of rainwater (solution chemistry from Hem, 1985) was modeled using Geochemist's Workbench, and pH was predicted to increase with reaction progress. The model results (Fig. 6) are in agreement with the assumption of White (1983) that dissolution of tephra will increase pH, at least while a fresh basaltic tephra source remains.

Ornithogenic soils at Miers Bluff

Soil formation by phosphatization reactions are likely at the MB raised beaches. The concentrations of total P found in ornithogenic soils typically ranges from 0.5-2.5% which is an order of magnitude higher than in non-ornithogenic soils. The MB raised beaches have average total-P concentrations greater than 1%. Lighter horizon colors and finer textures observed in the MB raised beaches are also indicative of ornithogenic soils (see L10 and L12 in Table 2).

The MB raised beaches however are in many respects similar to the USC raised beaches.

Both have statistically similar carbon and nitrogen values and both have an increase in total oxide iron and aluminum relative to the other soils as well as translocation of extractable iron and aluminum into subsoil, and both have relatively similar elevations above sea level. The major difference is a 10 fold increase in total-phosphorus in the MB raised beaches compared to the USC raised beaches. The question is thus posed as to the source of the phosphorus, mainly is the phosphorus derived from contemporary Skua guano or does the phosphorus represent a relict ornithogenic deposit of penguins deposited before uplift of the beaches to the present elevation?

Normally, high phosphorus loadings are associated with high carbon and nitrogen in the form of chitin and uric acids (Pietr *et al.*, 1983). Increased vegetation at the USC raised beaches also does not explain the similarities, as the MB raised beaches actually have more vegetative ground cover. In addition, total magnesium which is usually associated with fresh guano derived from seawater is significantly lower at MB than at USC. Calcium increases with depth until Ca:PO₄ is ~ 1:1, and is likely representative of a stoichiometric relationship from calcium phosphate. The nearly stoichiometric relationship of calcium and phosphorus in the MB raised beaches indicates that phosphatization reactions due to guano inputs have occurred. The loss of carbon, nitrogen and magnesium and the increase in calcium suggest the MB raised beaches contain relict ornithogenic soils. The production of noncrystalline materials released during rapid weathering of tephra also has the ability fix very high levels of phosphorus and since characterization of the phosphate minerals in these soils was not performed we are unable to say with certainty which process predominates. However, Tatur (1989) observed that relict ornithogenic soils and phosphate minerals were present hundreds to thousands of years later and that under neutral to alkaline conditions apatite-like minerals were quite common. This conclusion is contradictory to the findings of Emslie *et al.* (2010), who found it unlikely that

older, relict rookeries of the *P. papua* or *P. antarctica* existed to any great extent since their influx to the region appears to have been recent phenomenon (less than 1,000 yr BP).

Conclusions

Processes contributing to soil formation on Hurd Peninsula are identified and evaluated.

Chemical weathering is impacted by guano addition, and its effect was examined at a set of comparable geomorphic landforms, two similar sets of raised beaches, one of which is directly affected by ornithogenic conditions and another which is less so. Soils at Hurd Peninsula show large amounts of intermixed tephra throughout soil profile, and the oldest soils at the top of the raised beaches have accumulated a fine layered tephra mantle over time. Vegetation is not a major contributor to soil formation at Hurd Peninsula, because it doesn't occur to large extent.

Tephra deposition is concluded to be the primary mechanism driving rubification and soil formation, though guano deposition, which is spatially variable and temporally sporadic across the site, also contributes to chemical weathering through the addition of oxalic acid.

Phosphatization reactions are likely only significant at the raised beaches on MB. Geochemical modeling of tephra dissolution indicated that pore water pH increases in subsoil with dissolution.

Dissolution of silicates by phosphate is therefore likely not a major contributor due to unfavorably low temperatures, unfavorably high pH conditions and low phosphorous levels.

Experiments measuring dissolution of tephra under varying oxalic acid concentration and pH over time would aid in confirming the conclusions suggested in this study. Characterization of phosphate minerals and iron oxides in addition to additional geochemical modeling of mineral dissolution reactions may further refine the proposed model for soil formation at the site.

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426

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540

Table 1

TABLES

Profile	Elev- ation (m)	Slope (%)	Soil Depth (cm)	Plant Cover (%)	C (kg m ⁻²)	N	P	Landform ^a	Taxonomic Subgroup
Spanish Cove									
L05	4	1	> 50	50	0.50	0.13	0.11	rb	Typic Gelorthents
L06	5	0	> 50	30	0.34	0.14	0.09	rb	Typic Gelorthents
L07	6	0	> 40	30	0.35	0.10	0.07	rb	Typic Gelorthents
L08	8	1	> 45	5	0.35	0.08	0.09	rb	Typic Gelorthents
L09	12	0	> 50	10	NA	NA	NA	rb	Typic Gelorthents
L17	13	3	> 75	1	4.38	0.64	0.34	rb	Typic Humigelepts
L16	18	4	> 75	1	3.93	0.64	0.40	rb	Typic Humigelepts
L18	28	4	> 70	<1	9.50	1.27	0.88	rb	Typic Humigelepts
Mt Reina Sofia									
L19	279	5	54	3	2.07	0.35	0.13	nsc	Typic Haploturbels
Bulgarian Beach									
L01	137	9	38	50	0.70	0.22	0.12	sbl	Typic Haplorthels
L02	133	4	63	10	1.73	0.44	0.22	cs	Lithic Gelorthents
L03	35	7	> 60	50	0.31	0.28	0.17	m	Typic Gelorthents
L13	115	47	> 54	0	0.35	0.15	0.06	sbl	Typic Gelorthents
L14	144	7	47	0	1.25	0.58	0.35	nh	Typic Haplorthels
L15	44	0	> 60	0	2.87	0.35	0.52	m	Typic Gelorthents
Miers Bluff									
L10	23	2	62	6	5.23	1.20	12.1	mp	Typic Haploturbels
L12	26	0	> 75	10	4.19	0.69	6.65	mp	Typic Gelorthents

^a cs: congelifractate surface; m: moraine; nh: nivation hollow; nsc: nonsorted circle; rb: raised beach; rg: rock glacier; sbl: stone-banked lobe.

Table 2

Horizon	Depth (cm)	Munsell color (moist)	pH (H ₂ O)	EC (μS/cm)	Total C (%)	Total N	Total P	Clay	Silt	Sand	> 2mm
L01 Bulgarian Beach											
D	0-1	5YR 4/1	NA	NA	NA	NA	NA	NA	NA	NA	97
C1	1-8	5YR 2.5/1	6.51	20.9	0.184	0.053	0.026	3	5	92	60
2C2	8-38	10YR 3/2	6.74	16.6	0.165	0.053	0.031	5	11	84	65
2C3	38-43	10YR 3/2	7.03	17.0	0.179	0.055	0.027	6	12	82	80
L02 Bulgarian Beach											
D	0-1	10YR 3/2	NA	NA	NA	NA	NA	NA	NA	NA	70
C	1-16	5YR 3/2	6.56	18.1	0.138	0.053	0.022	3	6	91	5
2C1	16-40	10YR 4/3	6.74	26.5	0.317	0.064	0.031	5	12	83	2
2C2	40-63	10YR 4/3	6.9	17.0	0.146	0.049	0.029	4	25	71	45
3R	63+	NA	NA	NA	NA	NA	NA	NA	NA	NA	0
L03 Bulgarian Beach											
D	0-1	5YR 4/1	NA	NA	NA	NA	NA	NA	NA	NA	80
A	1-9	5YR 3/1	6.76	18.3	0.086	0.064	0.024	7	10	83	46
C1	9-20	5YR 3/2	7.26	12.6	0.095	0.062	0.025	3	7	90	56
C2	20-50	5YR 3/2	7.46	12.1	0.043	0.038	NA	2	3	95	66
C3	50-60	5YR 3/2	7.72	10.4	0.033	0.039	0.046	4	8	89	64
L05 Lower Spanish Cove											
A	0-5	10YR 3/1	4.96	115.3	0.532	0.076	0.042	3	3	95	50
C1	5-36	10YR 3/2	6.36	38.4	0.168	0.047	0.050	1	1	99	82
C2	36-50	10YR 2/2	6.5	43.3	0.124	0.055	0.043	1	2	97	91
L06 Lower Spanish Cove											
A	0-3	10YR 3/2	5.05	80.1	0.335	0.062	0.036	7	6	87	82
C1	3-24	10YR 3/1	6.14	27.9	0.185	0.046	0.036	5	4	91	83
C2	24-50	10YR 2/2	6.43	24.4	0.113	0.059	0.038	3	3	95	86
L07 Lower Spanish Cove											
A	0-3	10YR 3/1	4.62	96.0	0.233	0.062	0.057	6	5	89	85
C1	3-20	10YR 2/1	5.36	54.2	0.141	0.049	NA	4	4	92	85
C2	20-40	10YR 2/1	6.01	27.6	0.153	0.040	0.038	3	3	94	87
L08 Lower Spanish Cove											
A	0-5	10YR 3/2	5.71	32.5	0.253	0.052	0.038	3	3	94	87
C1	5-29	10YR 3/2	6.61	16.3	NA	NA	0.042	3	5	92	88
C2	29-45	10YR 3/3	6.71	15.5	0.182	0.039	0.050	3	3	94	89
L09 Upper Spanish Cove											
A	0-13	10YR 3/2	6.22	19.4	0.407	0.061	0.058	3	7	90	53
Bw	13-24	10YR 3/4	6.23	17.3	NA	NA	0.090	6	9	85	53
2BC	24-50	10YR 3/3	6.4	16.4	NA	NA	0.044	3	5	92	92
L10 Miers Bluff											
A	0-7	10YR 3/3	5.48	52.9	0.312	0.069	0.224	3	6	91	20
2Bw	7-18	2.5Y 4/4	6.56	19.0	1.111	0.196	1.619	17	26	57	5
3Ab	18-24	10YR 3/3	6.75	14.8	NA	NA	1.039	4	10	86	20
3C1	24-51	10YR 3/3	6.21	40.5	0.346	0.087	0.961	6	44	50	2

[illegible]

Table 3

	Unit	Spanish Cove (<12 m a.s.l.)	Spanish Cove (≥12 m a.s.l.)	Bulgarian Bay	Miers Bluff
pH		5.87b	6.73ac	7.13a	6.14bc
Total-C	%	0.220a	0.844b	0.159a	0.695b
Total-N	%	0.053a	0.115b	0.050a	0.122b
Total-P	%	0.043ab	0.070b	0.033a	0.991
Total-Ca	%	0.263b	0.445a	0.568a	0.663ab
Total-Mg	%	0.725a	0.840a	0.774a	0.332
Total-K	%	0.089ab	0.058a	0.072a	0.201b
Total-Na	%	0.125a	0.156a	0.158a	0.162a
Total-Al	%	7825a	16886b	12570ab	10050a
Total-Fe	%	12904a	18866b	17863b	15891ab
Fine Clay	%	0.83a	1.7a	1.2a	2.1a
Coarse Clay	%	2.6a	4.7ab	3.7ab	6.5b
Fine Silt	%	2.6	8.3a	6.6a	10.1a
Coarse Silt	%	0.9	5.4ac	4.2a	10.6c
Very Fine Sand	%	0.8	4.5ab	4a	9.4b
Fine Sand	%	4.7	11.3a	9.8a	12.7a
Medium Sand	%	16.8a	18a	14.7a	12.3a
Coarse Sand	%	32	21.8a	21.9a	16.9a
Very Coarse Sand	%	38.8a	24.4bc	33.7ac	19.8b
Coarse Frag. (<2 mm)	%	82.9	37.9a	48.8a	21.2a
Means with same letters do not differ significantly among areas at p = 0.05. Data analyses were performed using Tukeys HSD procedure with R (R, 2008).					

Figure 1

FIGURES

Deception Island

Hurd Peninsula

Figure 3

Figure 4

Soil Profiles of the Raised Beaches at Spanish Cove,
Hurd Peninsula, Livingston Island

Figure 5

Figure 6

Figure and Table Captions

Figures-

Figure 1: Site map of location of Livingston Island (upper right), Hurd Peninsula (lower right) and the sampling sites on Hurd Peninsula.

Figure 2: Backscattered Electron image of tephra from Deception Island (top) and Hurd Peninsula (bottom). Black interstitial material indicates epoxy matrix. Light gray is volcanic glass while elongated darker gray crystals are plagioclase. White crystals are olivine with some FeTi-oxides. The very large dark gray plagioclase in the Deception Island sample is a phenocryst which grew in the magma chamber prior to eruption; all of the other small crystals nucleated during the eruption and were frozen together with the quenched volcanic glass. Black circular features within the tephra are voids from vapor bubbles as dissolved gases exsolved due to the pressure drop as the volcano erupted and the magma traveled up through the earth's crust. Fields of view: Deception Island ~600 microns; Hurd Peninsula ~250 microns.

Figure 3: Binary comparison of oxides percentages in tephra samples from Hurd Peninsula (Red circles) and Deception Island (Blue Squares). Included is EPMA oxide analysis of Deception Island glass samples from Kraus *et al.*, 2012 (Blue dots, labeled DI-MaineDB).

Figure 4: Topochronosequence of soils on raised beaches at Spanish Cove. Artificial colors created with R using the aqp package (Beaudette, Roudier, & O'Geen., 2012).

Figure 5: Citrate-dithionite extractable Fe and Al on a topochronosequence of raised beach at Spanish Bay.

Figure 6: Geochemical model demonstrating the theoretical dissolution of 5 grams of Hurd

Peninsula tephra reacted with 100 L of rainwater.

Tables-

Table 1: Site and pedon characteristics for soils sampled during 2011 on Hurd Peninsula, Livingston Island.

Table 2: Analytical properties of pedons at Hurd Peninsula, Livingston Island.

Table 3: Means of the major nutrients and particle sizes by distinct areas at Hurd Peninsula.