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Surface mineralization on Seymour Island, Antarctica

ABSTRACT: Mineral composition of bedrock is the main factor determining salt mineralization in the weathering zone of Seymour (Marambio) Island (maritime — Antarctic continent climatic boundary). Supply of salts by sea water spray can accelerate weathering process, modify chemical formula of salt minerals and give ephemeral efflorescences of easy soluble chlorides and partially longer lasting gypsum on the surface. Microbiologically mediated oxidation of sulphides and followed acid sulphate drainage formed K and Na jarosite, basic amorphous aluminium sulphate, gypsum, aluminium bearing ferrihydrite and ankerite in weathering zone of Paleogene sediments. Intense alteration of well-lithified, calcareous sandstones of unit 1 of the López de Bertodano Formation (Cretaceous) on old erosion surface led locally to surface mineralization comparable with that found in Antarctic Continent. Stones laying on the soil surface are covered by thin red film of ferrihydrite above the soil level and by light green crust of aragonite coloured by glauconite pigment on the underground side. Most of the Cretaceous sediment does not contain sulphides nor alteration susceptible silicates thus ephemeral sea salts efflorescences observed on its surface are more prominent than in another places.

Key words: Antarctica, Seymour (Marambio) Island, weathering, mineralogy, microbiology.

Introduction

The occurrence of salts in soils and weathered rocks gives important information concerning the abiotic environment, and has a strong influence on the development of biota. Highly soluble salts are common on the Antarctic

Continent in subxeric, xeric, and ultraxeric soils and weathered bed-rock. Typically these salts occur as crusts on pebbles, blocks and solid rock, or as surface and subsurface accumulations (Vennum 1979, 1980, 1986, *in press*; Campbell and Claridge 1987; Vennum and Nishi 1981). The mineral composition and vertical distribution of these salts are the primary diagnostic features of these arid soils. Highly soluble salts do not occur in maritime Antarctica due to summer rains and high humidity. Precipitation there exceeds evaporation for a prevailing part of the year (Allen *et al.* 1967). Only slightly soluble salts such as carbonates and ornithogenic phosphates are found in this zone (Tatur 1989, Tatur and Keck 1990, Tatur and Sletten 1990).

Seymour Island (Fig. 1) lies at the boundary between maritime and continental climate zones. This paper reports the occurrence of sulphate, carbonate, chloride and hydroxide minerals in the surface bed-rock layer.

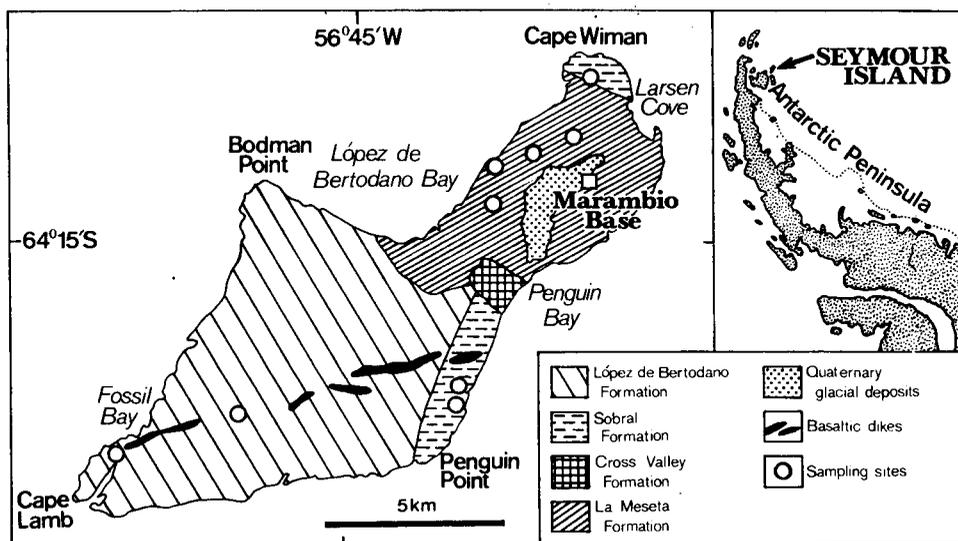


Fig. 1. Index map of Seymour Island according to Zinsmeister (1982), modified.

The presence of these minerals is not unusual in this near-continent area, but their abundance in some places is surprising. This is the first published record of salt mineralization on Seymour Island and the first consideration on microbiological participation in oxidation of sulphides in the weathering zone.

Methods

Surface soil and rock samples were collected from Seymour Island by the Argentine — Polish Field Party in 1985 and completed during Argentine

Antarctic Expedition 1992. Finest grain size classes (concentrating products of weathering minerals) were separated by sieving or sedimentation. Mineralized crusts were collected by scraping using a scalpel.

Sulphates, carbonates and hydroxides were dissolved in 10% HCl and concentrations of cations were measured in this solution by atomic absorption (excess La was added for determination of Ca and Mg). Sulphur, extracted by 10% HCl solution and total S by dissolution in aqua-regia, were determined by a gravimetric method (Bielopolskiy *et al.* 1974). The concentration of sulphur extracted by 10% HCl was similar to that extracted by aqua-regia, while the cations contents were higher in the latter, suggesting some extraction from silicate minerals. Therefore, the aqua-regia data are not presented in this paper. Several samples were extracted with CCl₄, but no elemental S was found by this method. Carbon and nitrogen were determined with a Carlo-Erba CHN analyzer, phosphorus-colorimetrically, and pH was determined in water suspension of soil (10 g of soil in 10 ml of water). The results are shown at the Table 1.

Minerals were identified by X-ray diffraction performed using a Dron-1 instrument with CuK_α radiation and a Ni filter. The X-ray source was set at 38 mV and 10 mA. The minerals were also observed by optical and electron microscopy. Micrographs were taken using a Jeol Ash instrument.

Isolation of autotrophic sulphur-oxidation bacteria of the genus *Thiobacillus* and sulphur-reduction bacteria of *Desulphovibrio* from soil was carried out in the laboratory to examine, if formation of sulphate mineralization in result of sulphide oxidation is mediated by microbiological processes in the investigated area. The following media, listed by Rodina (1965), were used in the cultivation experiment:

— Waksman medium for cultivation of bacteria *Th. thiooxidans*, controlling oxidation of elemental sulphur and thiosulphates.

— Silverman and Lundgren medium for cultivation of *Th. ferrooxidans*, bacteria controlling oxidation of thiosulphates and inorganic iron compounds (including sulphides).

— Beijerinck medium for cultivation of *Th. thioparus*, bacteria controlling oxidation of thiosulphates, sulphates and elemental sulphur.

— Trautwein medium for cultivation of *Th. denitrificans*, bacteria controlling oxidation of thiosulphates, sulphides and polysulphides to sulphates under anaerobic conditions.

— Postgate medium for *Desulfovibrio desulfuricans*, autotrophic bacteria controlling reduction of sulphates in anaerobic conditions.

Cultivation of bacteria cultures were conducted at constant temperature 28-30° C and under stationary conditions. The obtained mixed (non-ascenic) cultures were counted in Thom's chamber after 30 days of incubation.

Table 1

Chemical composition of surface mineralization.

Sample No	Cations dissolved in 10% HCl.									
	Fe	Ca	Mg	Na	K	Al	Mn	Zn	soluble part	S
	%	%	%	%	%	%	ppm	ppm	%	%
1 m	0.8	0.07	0.30	0.15	0.10	0.39	65	17	6.4	0.79
2 s	3.8	0.21	0.38	0.24	0.10	0.98	210	140	16.4	0.82
3 s	4.6	2.15	0.31	0.03	0.19	1.19	660	117	25.6	2.38
4 s	10.7	0.10	0.12	0.30	0.90	0.45	75	91	40.4	3.64
5 s	13.3	0.22	0.09	1.73	0.36	0.18	40	45	48.2	5.30
6 s	18.0	0.09	0.15	1.81	1.00	0.24	45	12	56.0	5.91
7 m	13.4	0.17	0.04	0.52	2.40	0.07	20	7	46.0	5.23
8 s	11.2	0.18	0.11	0.11	2.64	0.29	50	17	42.4	4.56
9 m	4.9	1.90	0.61	4.40	0.08	0.40	720	230	46.8	5.06
10 m	1.2	4.20	1.45	0.08	0.07	9.95	330	395	70.0	7.03
11 m	2.0	6.66	0.17	0.13	0.00	8.13	61	310	71.0	7.30
12 m	0.3	29.50	0.08	0.04	0.01	0.00	70	30	95.2	17.48
13 m	5.2	12.20	0.08	0.08	0.09	0.57	54	32	69.0	9.79
14 m	11.9	5.40	0.39	0.03	0.18	3.45	380	162	75.8	5.12
15 m	35.0	2.00	1.02	0.20	0.06	0.00	3500	180	60.4	0.05
16 m	4.7	25.20	0.41	0.16	0.19	0.40	500	170	85.6	0.00
17 m	1.6	1.30	0.21	2.90	0.08	0.40	100	140	16.2	2.03
Molar ratios										
4	3.37	0.04	0.09	0.23	0.41	0.50	—	—	—	2
5	2.88	0.07	0.04	0.91	0.11	0.14	—	—	—	2
6	3.50	0.02	0.07	0.85	0.28	0.16	—	—	—	2
7	2.94	0.05	0.02	0.28	0.75	0.06	—	—	—	2
8	2.82	0.06	0.06	0.07	0.95	0.26	—	—	—	2
9	0.56	0.30	0.16	1.23	0.01	0.10	—	—	—	1
10	0.10	0.46	0.27	0.02	0.01	1.71	—	—	—	1
11	0.16	0.70	0.03	0.03	0.00	1.35	—	—	—	1
12	0.01	1.35	0.01	0.00	0.00	0.00	—	—	—	1
13	0.30	1.00	0.01	0.01	0.01	0.07	—	—	—	1
14	1.33	0.84	0.10	0.01	0.03	0.80	—	—	—	1

Remarks: Enriched by (m) mechanical or (s) sedimental method

Concentration of C org < 0.2 %, N < 0.02 %, P < 0.3 %.

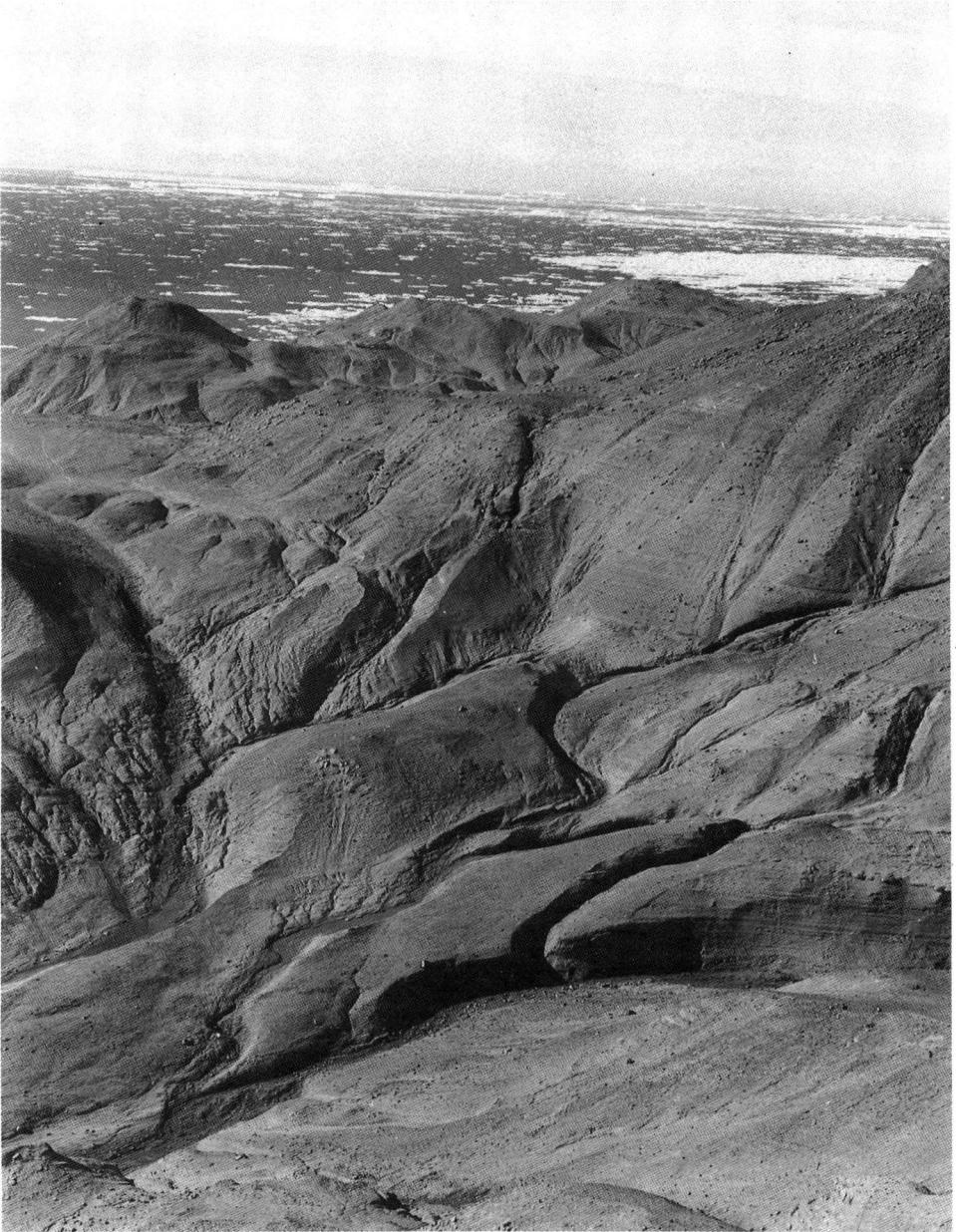
Description of samples presented in Table 1:

Samples from the Paleogene sediments (Sobral and La Meseta formations):

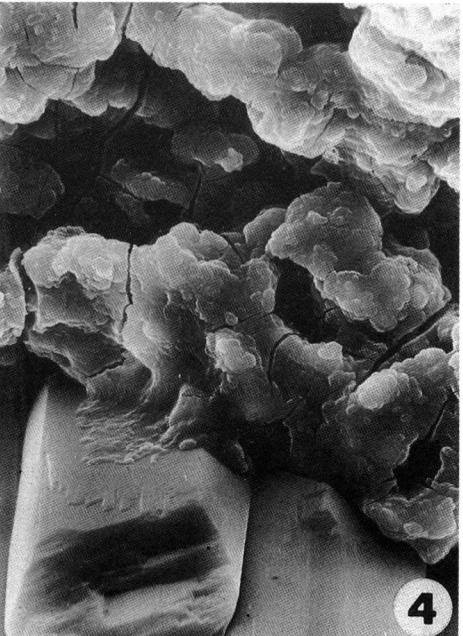
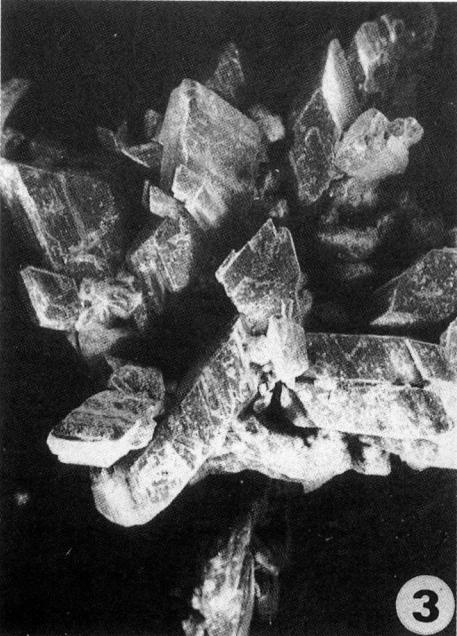
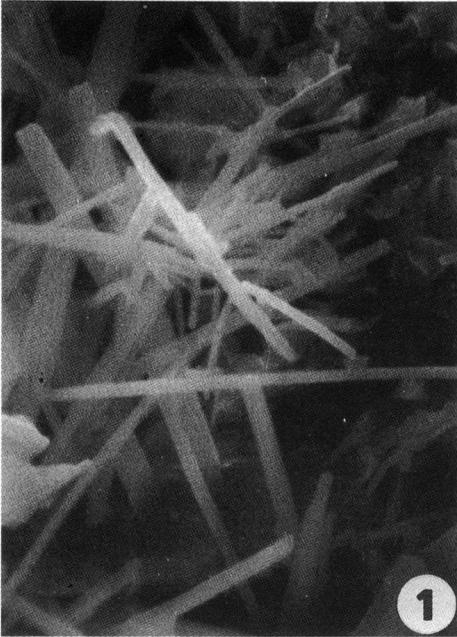
1 — gray silicate clay from weathering zone (background), 2 — brown silicate clay with admixture of iron hydroxides, 3 — brown silicate clay with admixture iron hydroxides and gypsum, 4 — yellow silicate clay with K > Na jarosite, 5 — yellow silicate clay rich in Na > K jarosite and with traces of gypsum, 6 — yellow silicate clay rich in Na > K jarosite, 7 — yellow silicate clay rich in K > Na jarosite, 8 — yellow silicate clay rich in K > Na jarosite, 9 — yellow silicate clay rich in undefined basic sulphate of Na > Fe > Ca with strong reflections 10.26 Å, 10 — white amorphous aluminium sulphate mixed with gypsum coating carbonate concretion, traces of carbonates are present, 11 — white amorphous aluminium sulphate coating carbonate concretion, traces of carbonates, 12 — light gray gypsum covering underside of carbonate stone, admixture of carbonates is present, 13 — brown—gray ferruginous bank, mixture of gypsum with ferrihydrite, 14 — brown ferrihydrite with gypsum admixture (ferruginous bank).

Samples from the Cretaceous strata (the López de Bertodano Formation):

15 — ferrihydrite coating upper side of stones (unit 1), 16 — aragonite coating underside of stones (unit 1), 17 — sea salt efflorescences (halite and traces of gypsum were identified by X-ray diffraction) mixed with clay. One of many little pools common on the soil surface.







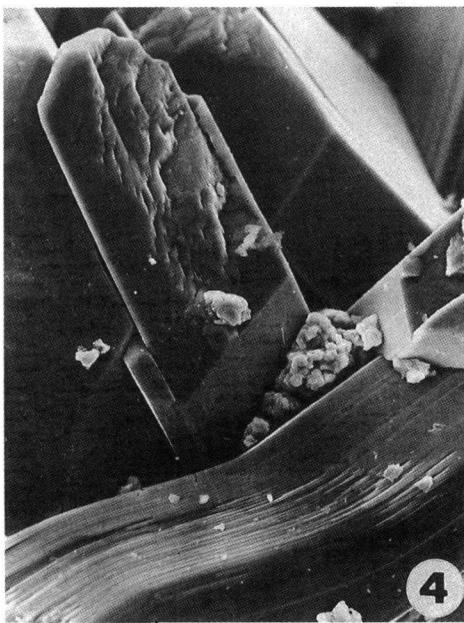
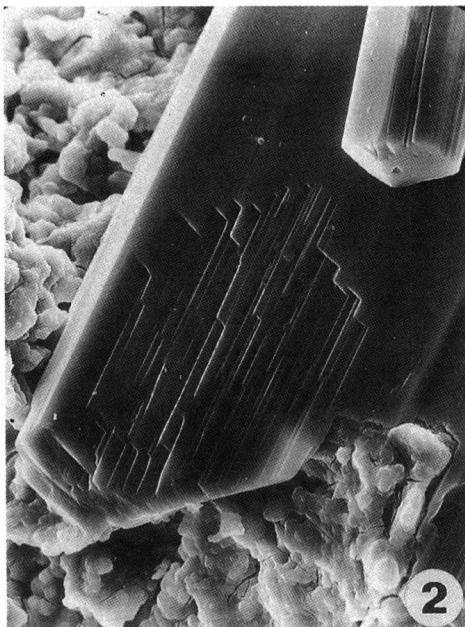
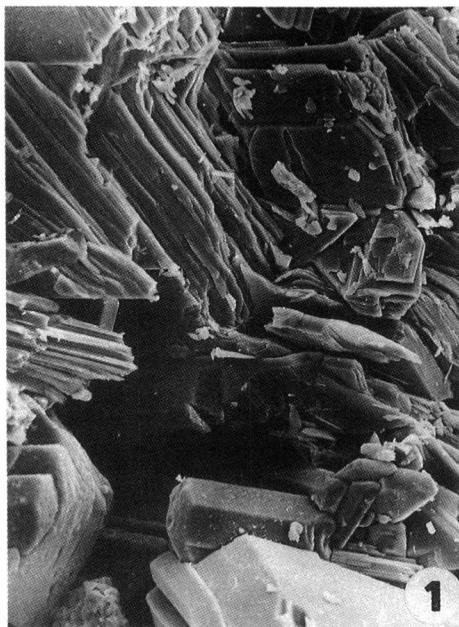


PLATE 1

Geomorphology typical of the area built of sandy marine rocks of the middle part of the La Meseta Formation. Seymour (Marambio) Island, Antarctic Peninsula. Photo taken by A. Gaździcki, January 1988

PLATE 2

Gravelly surface formed by the weathering process of *Cucullaea* shell banks exposed in the highest part of sea cliff in the López de Bertodano Bay. Unit II of the La Meseta Formation. Seymour (Marambio) Island, Antarctic Peninsula. Photo taken by A. Gaździcki, January 1988

PLATE 3

Fig. 1. Well defined habits of unidentified minerals crystallized from extract of jarosite-rich sample during prolonged to one month measurements of pH in H₂O. The La Meseta Formation. SEM × 3700

Fig. 2. Gypsum: minute roses of desert found in loose sand of the La Meseta Formation. SEM × 70

Fig. 3. Micro-crystals of gypsum in the weathered zone of loose sand of the La Meseta Formation. SEM × 60

Fig. 4. Ferrihydrite and gypsum: main components of ferruginous bank. The Sobral Formation. SEM × 2000

PLATE 4

Fig. 1. Locally corroded gypsum crystals in ferruginous bank of the Sobral Formation. SEM × 240

Fig. 2. Crystals of gypsum with amorphous ferrihydrite in the background. Ferruginous bank of the Sobral Formation. SEM × 780

Fig. 3. Idiomorphous crystals of gypsum forming frame in ferruginous bank of the Sobral Formation. SEM × 72

Fig. 4. Plastic deformation of gypsum crystals in ferruginous bank of the Sobral Formation. SEM × 300

Geological description of study site

Seymour Island (Fig.1) is formed from sedimentary rocks originating in Lower Tertiary and Upper Cretaceous cut by basaltic dikes (Zinsmeister 1982, Elliot and Trautman 1982, Sadler 1988). To the Paleogene belongs: Sobral, Cross Valley, and La Meseta formations. All three of these formations occur as loose light sand often with glauconite, intercalated in changeable ratios with dark gray bituminous silts and clays bearing sulphides (Pl. 1). Carbonate concretions, of various shapes, are prevalent in several levels of the Paleogene rocks, particularly in the fossil rich La Meseta Formation (Pl. 2).

The Cretaceous loose silts and sands (well lithified at the base only), represented by the López de Bertodano Formation (Macellari 1988), are generally more homogenous (less distinct interbedding) and lighter when weathered (less content of bitumens and sulphides).

Geomorphological description of study site

The sandy Paleogene sediments are overlain by a thin horizontal sheet of till forming a flat plateau that rises to 200 m a.s.l. in the northeast part of the island (Figs 1—2). The loose sandy slopes of plateau have been washed by water erosion, leaving a gravelly surface (Pls 1—2). Classic water-eroded V-shaped valleys with steep walls have been formed. The Cretaceous sediments are also graveled by erosion, however, topography is more disintegrated and diversified, many local flat patches with periodic pools occur. Only well lithified sandstone of Lowermost Cretaceous and basalt dikes form prominent cuesta topography.

The surface of Seymour Island is almost completely devoid of vegetation. There is no accumulation of soil organic matter in the recent soil forming processes. However, bituminous compounds inherited from the bedrock can occur in weathering covers.

Results

Mineralization in weathering zone of the Paleogene sediments. — Surface salt mineralization is formed here clearly due to oxidation process of iron sulphides concentrated in bituminous silty — clay intercalations common in sandy sediments of the Paleogene. Salt mineralization occurs only in the parts of rock rich in dark silty clay, which during graduate weathering becomes a little violet with strong acid reaction and finally yellow clay rich in jarosite is produced as lenses and trails inside and around the weathered layer. Yellow clay changes colour to brown with increasing distance from place of oxidation and iron hydroxides sometimes with aggregates of gypsum crystals (minute roses of

desert) appear as important clay component there. Violet-yellow-brown bands marking mineral zonation of sulphides oxidation zone are commonly observed in sediments which still retain its sedimentary structures. Large part of the land is washed off to the solid rock exposure, thus that mode of occurrence is common on Seymour Island.

However, acid drainage, always connected with sulphides oxidation in environment wet enough, usually causes dissolving of previously formed salts and followed vertical and horizontal movement of ions in solution leading to new, secondary mineral formation in another places. Sulphate drainage zone penetrates irregular sedimentary rocks several metres down to the permafrost, that can be splendidly observed (1—4 m deep) in fresh cliff at the W-N end of island, while horizontal transport of solutions on land is limited by contemporary topography only.

Accumulation of brown iron hydroxides sometimes bearing gypsum frequently occurs in soil like illuvial horizons under light, leached sand or under jarosite-rich sand layer. Several times the following sequence was found proving that solutions derived in result of acid sulphate drainage and percolating down through loose sand are neutralized often by carbonates: at the surface — yellow, jarosite-rich sand, in the middle — brown, sand indurated by iron hydroxides and at the base — carbonate shell banks often with gypsum mineralization in the upper part. Usually opposite vertical order is observed in the soils elsewhere, from iron hydroxides on the top, jarosite in the middle and sulphides at the bottom of the soil (Breemen 1975). Accumulation of pure crystalline gypsum was found occasionally in indurated petrocalcic horizons. These are irregular, no more than few cm thick and two metres across.

Thick, erosion-resistant, brown coloured banks of sand indurated by iron hydroxides and gypsum are a special case of mineralization found in this area, especially well developed near Penguin Point (Fig. 1). Gypsum forms a hard crystalline frame, which contains inside mixture of iron hydroxides rich in aluminium plus sand. Pure gypsum concentrates also inside the banks as druse covering walls of cracks developed often along previous sand lamination. These ferriferous banks are up to 40 cm thick and may reach several metres in width. They were probably formed local in depressions that gathered and neutralized iron-bearing solutions of acid sulphate drainage. Subsequent erosion process must have removed the loose sandy surrounding and exposed the hard banks on the top of local mounts, thereby leading to an inversion of morphology.

The Paleogene sediments are full of stones, carbonate concretions and fossils (shells and bones). Gentle iron hydroxide staining on the above soil laying side and crystalline crust of gypsum occur sometimes on the underside of debris laying on the old stable erosional surface, often on the top of hills. A thin crust of gypsum can be frequently found also coating all over carbonate concretions and fossils occurring inside the weathering zone. Gypsum forms a druse with perfect developed crystals on the surface or inside splits.

Sometimes a film of soft snow-white, powder-like amorphous aluminium sulphate with variable gypsum admixture can be observed on carbonate debris. Iron hydroxides also often form lags around carbonate concretions and fossils. Ankerite — a common mineral of surficial deposits over sulphide ores was found in weathered soft zone of calcite concretions.

Efflorescences of sea water salts occur for short period of time in area of the Paleogene sediments. However, they are not so prominent like on the Cretaceous rocks, because of masking effect by dominating sulphide — hydroxides mineralization and because of geomorphology provided well drainage. Surface mineralization composed of carbonates, if existed, is not easy to recognize, because carbonates in variable forms occur also originally in the rock.

Microbiological activity of weathered covers and soils derived from the Paleogene rocks. — Numbers of cultivated bacteria connected with mineral sulphur transformations were highest in the samples rich in sulphides (Table 2,

Table 2

Abundance of microorganisms and pH values in selected soils and weathered rocks derived from silty sands of the La Meseta Formation.

Sample number	pH in H ₂ O	<i>Th. thiooxidans</i>	<i>Th. ferrooxidans</i>	<i>Th. thioparus</i>	<i>Thiobacillus denitrificans</i>	<i>Desulfovibrio desulfuricans</i>
1	2.5	6.4 x 10 ⁶	8.8 x 10 ⁶	8.0 x 10 ⁶	1.6 x 10 ⁶	2.4 x 10 ⁶
2	3.0	6.4 x 10 ⁶	8.8 x 10 ⁶	1.8 x 10 ⁷	1.6 x 10 ⁶	5.6 x 10 ⁶
3	3.0	6.4 x 10 ⁶	1.1 x 10 ⁷	1.3 x 10 ⁷	2.6 x 10 ⁷	2.9 x 10 ⁷
4	4.0	4.0 x 10 ⁶	1.4 x 10 ⁶	8.8 x 10 ⁶	2.3 x 10 ⁷	3.0 x 10 ⁷
5	3.4	8.0 x 10 ⁵	3.2 x 10 ⁶	8.0 x 10 ⁶	3.2 x 10 ⁶	2.4 x 10 ⁶
6	6.7	8.0 x 10 ⁶	1.6 x 10 ⁶	4.0 x 10 ⁶	1.6 x 10 ⁶	2.4 x 10 ⁶

Description of samples presented in Table 2.

1 — black — silty clay intercalation of bed-rock in the weathered zone (subsurface layer), 2 — black with violet colouration — silty clay intercalation of bedrock in the weathered zone (subsurface layer), 3 — yellow — jarosite mineralization in the glauconite rich sand (soil surface). Soil profile over shell bank, 4 — 0-5 cm, yellow — jarosite rich sand bearing glauconite (surface of soil), 5 — 5-10 cm, orange — mixture of jarosite plus iron hydroxides in sand, 6 — 10-50 cm, brown — iron hydroxides mineralization impregnating carbonate concretions.

nos 1–2) and in glauconite sand rich in jarosite (Table 2, nos 3–4), but lowest in the carbonate sand with neutral reaction (Table 2, no. 6). Microbiological activity is much higher than usually ascertained in soils, however, lower than that from soils polluted by sulphur mining (*after* Kobus 1980). It can be considered as very high, taking into account almost abiotic soil environment and severe climate in the searched place. Presented data prove that sulphur cycle in soils and weathered covers on Seymour Island is mediated by microbiological activity.

Samples representing the first steps of sulphides oxydation are characterized by very low pH values, even below 2, on prolonging contact with water and increasing bacteria population. At the end of the carried pH experiment (after one week) thick yellow to white precipitates appeared on the edge of vessel. X-ray analyses show crystallization of mineral associations comprising a mixture of common and rare sulphates (see next chapter). All these minerals could be formed in the field after each rain and probably they did — as surface unstable micro-efflorescences noted in form of a film on sulphide- or jarosite-rich samples.

Mineralization in weathering zone of the Cretaceous sediments. — The Cretaceous sediments of the López de Bertodano Formation build southern part of the Seymour Island (Fig. 1), where they form morphological features generally comparable to the northern, Paleogene part. Also basic petrographic composition of both formations is similar, except for sulphides absence in the finest grain size fractions of the Cretaceous sediments. Therefore, nowhere signs of sulphide oxydation and acid sulphate drainage was noted in the weathered zone and so surface sea water salt efflorescences are more prominent here than in another places. Formation of that mineralization is supported also by specific details in morphology — more flat nondrained areas on the Cretaceous bedrock than on Paleogene one, that means better conditions to collect sea water sprayed all over the island by strong wind. Thin ephemeral efflorescences of white, water soluble salts occur on the edges of periodically drying small pools, common in local nondrained depressions where they are lasting to the first rain. Near the coast of the sea sodium chloride dominates in salt (halite was identified by X-ray analysis), inland salts are less abundant and "more bitter" — probably higher in magnesium salts.

Special case of surface mineralization concentrates in the very narrow near sea cliff exposure of unit 1 of the López de Bertodano Formation at Fossil Bay (Fig. 1). Morphologically, unit 1 presents a prominent cuesta topography, fastened additionally by basaltic dike cutting the Cretaceous sediments in this place (Macellari 1988). Debris of well lithified calcareous sandstones, usually several centimetres in diameter, is scattered over several hundred metres along gentle slope being an old erosion surface. Our petrographic examination of thin sections indicates that clastic material in that sandstones is composed mainly of limestones containing glauconite and sandy intercalations of quartz, alkaline feldspars and acid volcanic rock fragments. This material released from limestones form finer clastic grain size classes in the rock. Pieces of sandstones when altered on the surface are covered by hard crust: red on the side over the soil and light green on the underground side. The red staining (developing locally to film or crust) is formed in outer part of rock by few mm thick concentration of amorphous to X-ray iron hydroxides (ferrihydrite), a little thicker light green crust is formed on underground side of the pieces of rock by

fine crystalline aragonite with two-valence-iron-bearing green pigment. It is rather obvious that the observed mineralization was formed in result of weathering of clastic material of the rock: limestones-affected underside carbonate mineralization, and glauconite-affected staining of stones above the soil surface. Additionally, long lasting alteration of rocky debris on the stable old erosion surface and constant supply of sea water spray could support that case of local mineralization.

Weathering products of sandstones (ferrihydrite, aragonite and chlorides) concentrate also in loams surrounding rocky ridge. Segregation of material in drying, freezing and washing processes can lead one of them to a local segregation, and red-green-white (sea salt) lining of mudcracks, and polygonal, solifluction and fluvial structures.

Identification of minerals formed in weathering process. — Mineralization on Seymour Island consists of sulphates (jarosite, gypsum, amorphous aluminium sulphate, ephemeral water soluble sulphates), carbonates (?calcite, aragonite, and ankerite) amorphous iron hydroxide (ferrihydrite) sometimes rich in aluminium, and chlorides — among them only halite was identified.

Jarosite $(K,Na)Fe_3[(OH)_6(SO_4)_2]$, identified on the basis of typical X-ray diffraction pattern, occurs in range of compositions, from a Na rich form (approximately 90% Na and 10% K in the alkalis site) to a K rich form (approximately 5% Na and 95% K in the alkalis site) (Table 1, nos 4-8). It is the primary component (comprising up to 50% of the bulk) of the yellow clay formed in the weathered zone directly in result of sulphide oxidation often still inside bituminous silty clay intercalations of the bed-rock. Crystals of jarosite were too small to observe, either by optical or scanning electron microscopy. Its occurs as an earthy aggregates in mixed with silicate clay comprising about 50 per cent of the sample (acid insoluble part in chemical analyses on Table 1). Potassium-rich jarosite usually occurs deeper inside the weathered zone of rock, while Na-rich forms are more common on the surface, especially in close proximity to the sea. There is common opinion that jarosite is formed when sulphides oxidize in an environment scarce in basic cations (Kobus 1980).

Surficial, yellow, crystalline efflorescences of pure salts can be occasionally observed in microscale. These field occurrences were, however, usually too small to be analysed and tested by X-ray. One collected sample of such mineralization gave undefined Na-Fe-Ca sulphate (or mixture of sulphates — Table 1, no. 9) with an unknown prominent X-ray diffraction pattern (10.26 Å). Minerals comparable to the considered field micro-occurrences have been probably obtained during prolonged to one week water pH measurements in laboratory. Yellow to white efflorescences of halite, jarosite and gypsum mixed with water soluble unstable sulphates: natrosiderite, hexahydrite, tamarugite (identified on the basis of the typical X-ray diffraction patterns) crystallized on the edge of vessel from evaporating water suspension (Pl. 3, Fig. 1).

Crystalline gypsum is found in a variety of environments: minute desert roses in loose sand (Pl. 3, Figs 2–3), surficial crust on carbonate concretions and fossils, druses covering underside of stones laying on the surface, petrocalcic horizons, and in ferruginous banks (Pl. 3, Fig. 4; Pl. 4, Figs 1–4). Gypsum was identified on the basis of the typical X-ray diffraction patterns, microscopic observation (Figs 7–11), and chemical analyses of almost pure occurrence of this mineral (Table 1, no. 12). Euhedral crystalline shapes with multiple twins are common in almost all cases, however, especially clear form of crystallization with multiple twinning can be seen on Pl. 4, Fig. 3. Sometimes plastic deformation (Pl. 4, Fig. 4) and signs of existence in environments where gypsum was the subject of corrosion conditions, were observed (Pl. 4, Fig. 1). Differentiated occurrences suggest that gypsum may form under a variety of physical and chemical conditions including precipitation from evaporating sea-water, or as the result of acid sulphate drainage of carbonates.

Iron hydroxides also occur in a variety of environments including participation in secondary clay (Table 1, nos 2–3), staining, crust and lags on carbonate concretions, carbonate sandstone debris (Table 1, no. 15) and fossils, forming illuvial soil horizons resulted from acid sulphate drainage, and as an iron-rich matrix in indurated sand banks (Table 1, nos 13–14). In all tested cases the iron hydroxides are amorphous according to X-ray diffraction data and under light microscopy, and on SEM images (Pl. 3, Fig. 4; Pl. 4, Fig. 2). This is assumed to be ferrihydrite since this is generally believed to be the primary form of amorphous iron hydroxide mineral occurring in soils (Schwertmann and Taylor 1989). Calculation of molecular ratios in sample of ferriferous concretion (Table 1, no. 14) reveals that even if some part of aluminium can form sulphate (some excess of sulphur in relation to normative gypsum) there is still significant part left, which probably substitute for Fe in hydroxides or participate in an amorphous mixture of iron and aluminium hydroxides. Iron hydroxides rich in aluminium may precipitate from acid solutions leaching silicates (for example common glauconite in the Paleogene rocks). Whereas, ferrihydrite crust formed on debris, where acid drainage does not occur, is free of aluminium.

Amorphous aluminium sulphate occasionally occurs as a relatively pure thin film of soft, white, clay-like material covering carbonate concretions. Chemical analysis (Table 1, nos 10–11) and X-ray diffraction data suggest that it consists of a basic amorphous mineraloid. An exact formula is difficult to calculate because it is mixed with silicates, gypsum, and some of carbonates. This mode of occurrence seems to be typical. Precipitation of basic aluminium sulphate often occurs when solution bearing aluminium and sulphate ions comes into contact with carbonates (Hollingworth and Bannister 1950) and neutralization of its acid reaction occurs (Bloomefield and Coulter 1973).

Probably comparable basic aluminium sulphates hydrolyzed quickly to crystalline aluminium oxides, was obtained in laboratory experiments designed to simulate acid sulphate weathering (Johansson 1962). However, no signs of this process were found in the searched conditions.

Carbonates are common especially in the Paleogene rocks and their weathering origin is sure only sometimes. Fine crystalline almost pure aragonite crust (Table 1, no. 16) on the Cretaceous carbonate sandstones of unit 1 belongs to such case. Aragonite was determined on the basis of typical X-ray data. Carbonates that occur as thin films on weathered calcite concretions, in the area of acid sulphate drainage in the Paleogene sediments, in two cases were found to be ankerite — a common mineral in surface deposits of sulphide ores. Therefore, weathering origin of this mineral seems to be likely. However, it is difficult to discuss weathering origin of secondary calcite since it is common in the rock background there.

Discussion

Oxidation of sulphides in weathered covers and soils (Fe/S 1) could lead to jarosite (Fe/S 1.5) formation leaving an excess of sulphur as sulphuric acid that may react with carbonates and silicates (possible reaction with glauconite — Pons and Kevie 1969) to form gypsum, aluminium sulphates, and jarosite or iron hydroxides and sometimes ankerite in the process of jarosite alteration. This sulphate, hydroxide and carbonate mineralization is similar to those occurring locally in oxidized caps above sulphide ore outcrops in many places of Antarctic continent (Kaneshima, Torii and Miyahira 1973; Hirabayashi and Ossaka 1976; Vennum 1980; Vennum and Nishi 1981), and also in many other environments all over the world: in rice soils of Vietnam (Warshaw 1956), in soils of tidal swamps (Pons and Breemen 1982), in soils supplying by salt ground water along Baltic sea coast in Poland (Pracz 1989), mining wastes in Ohio (Bigham *et al.* 1990), in oxidized caps above sulphide ores in Andes (Bandy 1938, Cook 1978), deserts and elsewhere as a less important component of clays derived from sulphide bearing rocks.

Sulphur bacteria control sulphide oxydation all over the world wherever sulphide rich ores, soils or slugs occur (Jensen 1927, Breemen 1975, Kittrick *et al.* 1982, Bigham *et al.* 1990). Severe climate of Seymour Island have not excluded microbiological activity and sulphur cycle in weathered zone there (and probably also on Antarctic continent) is mediated by microbiological processes. Possible abiotic oxydation of pyrite suggested as important in some cases by several authors (Harward and Reisenauer 1966) can be no more considered as the only factor responsible for mineral sulphur transformation in Antarctic environment.

Therefore, iron and aluminium sulphates that are common on Seymour Island may be considered to be azonal, forming wherever acid sulphate drainage takes place. Gypsum indicates that conditions are generally arid, however, it is moist enough for iron — aluminium hydroxides to form and to prevent the stable accumulation of chloride and nitrate salts. The abundance of sulphates is more prominent in common Paleogene sediments of Seymour Island than in other areas of Antarctica with the exception of oxidized caps of sulphide ore deposits. The reason for this is undoubtedly related to sulphides abundance in the bedrock. Water related weathering processes are, however, intense enough to oxidize sulphides, but too weak to result in strong silicate weathering in sedimentary rock (except for acid sulphate drainage effects), and leaching of sulphuric acid excess from soil environment seems to be ineffective, that prevent probably to a high degree development of vegetation. Therefore, solely oxidation of sulphides and then transformations of sulphur compounds can be considered as the initial soil forming processes in this area.

On the Antarctic continent, the occurrence of sulphate minerals may also be due to sulphur originating in sea-water (sea-water contains approximately 900 mg S dm⁻³) (Polański and Smulikowski 1969). Sulphates may be carried to land by sea spray or as trapped bodies of sea water during sea level changes or isostatic rebound. Salt minerals (chlorides, mirabilite, gypsum) on the coast of the continent are derived from sea-water according to stable isotopes studies of sulphur and oxygen (Lyon 1978, Bowser *et al.* 1970, Nakai *et al.* 1978). The most spectacular explanation is the derivation of sulphur from the surface of tropical oceans, as described by Wilson (1959), and transportation to the polar regions in the upper atmosphere (Fisher *et al.* 1969, Machaut *et al.* 1979) by the permanent anticyclone that is centred over the Antarctic Continent (Campbell and Claridge 1987). Nitrate and sulphate mineralization in ultraxeric and xeric soils of the Antarctic Interior have been proposed to form in this way (many examples are given by Campbell and Claridge 1987). Another explanation according to Aristarain, Delmas, and Briat (1982) is that the enhanced concentration of sulphate relative to chlorides in the ice cap on James Ross Island (10 km north from Seymour Island) originates from oxidation of gaseous sulphur compounds produced by marine organisms in the surrounding seas.

The atmospheric origin of surface mineralization is according to our data of less importance on the wetter Seymour Island. Most of the white sea salts observed sometimes on the surface are used to be quickly dissolved in rain and melting waters, however, genesis of gypsum in result of evaporation of sea spray (as a less soluble sea salt) cannot be excluded, especially in the typical of Antarctic continent mode of occurrence — as a crust on under side of isolated from the bed-rock carbonate stones laying on the surface. Sea spray affected without any doubt jarosite composition commonly substituting Na for K in molecular formula, as well as, forming ephemeral, water soluble sodium rich sulphates in jarosite weathering zone.

Mineralization dominating in weathered zone of well lithified carbonate sandstones (unit 1 of the López de Bertodano Formation) forming in the landscape a *cuesta* with old erosion surface on the slope, occurs in different mode than in younger part of the Cretaceous and Paleogene sediments. Ferrihydrite film on the above ground side of clasts reminds that of Antarctic continent (Campbell and Claridge 1987) occurring commonly during long lasting surface weathering of rocks. Carbonate — calcite encrustations are also locally common on Antarctic continent, wherever weathering of carbonate-bearing rock took place. However, aragonite has not been reported yet in such case (Campbell and Claridge 1987). Precipitation of aragonite encrustation instead of calcite one may result from magnesium ion rich solution formed during weathering with constant supply of magnesium-bearing sea water spray supply. Magnesium ions can promote aragonite formation (Sletten 1988). The only comparable local occurrence of carbonates in the weathering zone of maritime Antarctica was noted by the first author of the present paper on Deception Island (near old whale hunters base). It forms calcite crust covering underside of hard, yellow tuffs, exposed in the outcrop near the shore of sea bay in caldera.

Most of the Cretaceous sediment does not contain sulphides nor alteration susceptible minerals thus sea salts efflorescences observed on its surface are more prominent than in another places. Sea salts can form thick and long lasting accumulations in dry Antarctic continent, however, they can be considered as ephemeral on more wet Seymour Island, because each one rain can dissolve it.

Conclusions

Weathering process in the cold mixed maritime-continental climatic conditions of Seymour Island affects mainly minerals most susceptible to alteration sulphides (microbiologically mediated process) and carbonates. Lack of easy weathering minerals on most part of the Cretaceous sediments promote better exposing of ephemeral sea salt efflorescences. Clear relationship among mode of weathering and mineral composition of bedrock proves that atmosphere-related sources of mineralization suggested as main ones for Antarctic continent, are less important in the case of Seymour Island.

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Streszczenie

Wyspa Seymour znajduje się pomiędzy morską a kontynentalną strefą klimatyczną i mineralizacja tu występująca ma również charakter przejściowy choć bardziej zbliżony do mineralizacji na kontynencie niż na wyspach po zachodniej stronie Półwyspu Antarktycznego zaliczanych do Antarktyki morskiej (fig. 1, pl. 1–2). Mineralizacja została udokumentowana metodami chemicznymi (tab. 1) rentgenograficznymi oraz badaniami przy użyciu mikroskopów polaryzacyjnego i scanningowego (pl. 3–4).

Procesy wietrzenia na Wyspie Seymour atakują selektywnie podatne na rozkład minerały: siarczki w osadach paleogeńskich, węglany i glaukonit w przypadku piaskowców najniższej kredy. Natomiast brak łatwo wietrzejących minerałów w skale, pozwala lepiej zauważyć mineralizację solną spowodowaną przez aerozol morski przyniesiony na ląd przez silne wiatry. Obserwacje te jednoznacznie wskazują, że mineralizacja powierzchniowa tworzy się na Wyspie Seymour przede wszystkim w procesie wietrzenia skał i pozostaje w ścisłym związku ze składem mineralnym skały macierzystej. Natomiast bryzgi wody morskiej nawiewane na ląd mogą modyfikować skład chemiczny mineralizacji wietrzeniowej, przyspieszać sam proces wietrzenia i tworzyć powszechnie efemeryczne powierzchniowe wykwity soli morskich, które za wyjątkiem gipsu są łatwo rozpuszczalne przez deszcze i wody roztopowe. W strefie kontrolowanego przez mikroorganizmy (tab. 2) wietrzenia zawierających siarczki skał paleogeńskich (kwaśny drenaż siarczanowy), stwierdzono różnorodne formy występowania jarosytu, gipsu, amorficznych zasadowych fosforanów glinu oraz niewielkie ilości innych nietrwałych, krystalicznych siarczanów o urozmaiconym składzie kationów. W wyniku wietrzenia siarczanów żelazistych i glinowych powstają powszechnie nagromadzenia bogatych w glin wodorotlenków żelaza (ferrohydrat) i niekiedy węglany (ankeryt), wskazujących jednoznacznie na istotną rolę wody w procesach wietrzeniowych. W strefie wietrzenia piaskowców węglanowych leżący na powierzchni gleb rumosz skalny pokryty jest na wierzchniej stronie bezglinowym ferrohydratem a aragonitem na stronie spodniej.