POLISH POLAR RESEARCH | 8 | 1 | 65—74 | 1987

Andrzej TATUR

Institute of Ecology
Polish Academy of Sciences
Dziekanów Leśny
05-092 Łomianki, POLAND

Fluorine in ornithogenic soils and minerals on King George Island, West Antarctica

ABSTRACT: A high content of fluorine was found in ornithogenic soils around penguin rookeries on King George Island, South Shetland Islands. Fluorine is inherent in 0.11% in krill (*Euphausia superba*), eaten by penguins. Fluorine content in penguins excreta increased approximately to 0.43%, and after decomposition and leaching to 1.03%. The concentration grew during mineralization of organic matter in guano (up to 2.2%). In a surface layer of guano fluorine occurred in apatite. A phosphatization was noted in a subsurface zone as the result of a reaction between guano leachates and weathered volcanic rocks. In the upper part of this zone near the large rookeries a fluorine occurred in minyulite (aluminium phosphate containing potassium and fluorine) and fluorine content here reached 3.5%. Sometimes fluorine was also bound with amorphous aluminium phosphate (up. to 2.0%), formed as a result of incongruently dissolving of minyulite in pure water.

Key words: Antarctica, geochemistry, ornithogenic soil, phosphates, fluorine.

Introduction

Fluorine readily combines with calcium phosphates and sometimes high concentrations of fluorine have been also reported from ornithogenic deposits composed of phosphatic guano (Hutchinson 1950, White and Warin 1964, Altschuler 1973, Emigh 1973). According to these authors, fluorine came from sea spray carried on land by winds and it was probably of a post-depositional origin. A preliminary determination of fluorine made in a sample of phosphate from the ornithogenic soil on King George Island (maritime Antarctic), indicated also a high content of this element (Tatur and Barczuk 1984). However, the food of penguins and not a sea spray was most probably the primary source of fluorine in this region. Penguins in rookeries in the vicinity of King George Island belong to two species: Adelie (*Pygoscelis adeliae*) and Chinstrap (*P. antarctica*). These species feed almost exclusively on krill (*Euphausia superba*) during the austral summer while breeding (Volkman, Presler and Trivelpiece 1980). Krill contains 0.1149$\%_0$ of fluorine (Buchholz 1983) and several hundred tons of excreta are deposited annually on each large penguin rookery (Tatur and Myrcha 1984).

The primary aim of the study was to learn how fluorine interacts biogeochemically at the land/sea boundary in the maritime Antarctic. Especially the fluorine bearing minerals were identified and the concentrations of fluorine at different depths within ornithogenic soils were examed.

Methods

Samples of ornithogenic soils and minerals from King George Island were taken during IV Polish Antarctic Expedition under a leadership of Professor A. Myrcha (1979/80). The minerals and soils were described earlier by Tatur and Barczuk (1984), Tatur and Myrcha (1984).

A determination of fluorine has been made in the Institut für Meereskunde (Kiel, West Germany) by Borys Culik and Axel Keck from the staff of Professor Dieter Adelung. The sample was decomposed and fluorine concentrated by microdiffusion procedure according to method of Bäumle and Glinz in modification of Culik. Determinations of fluorine were carried out by colorimetric method according to Kremling in modification of Keck. Most of the remaining data were taken from the former publications of the author (Tatur and Barczuk 1984, Tatur and Myrcha 1984).

Results

The penguins feed on krill containing about 0.1149$\%_0$ of fluorine (Buchholz 1983). The concentration of fluorine increased in penguin excreta (0.42 — 0.45$\%_0$), in decomposed and leached penguin excreta (0.6 — 1.9$\%_0$) and finally in guano (up to 2.3$\%_0$), forming a thin superficial veneer around breeding places (Tables 1–2).

Fluorine of guano was usually bound to calcium phosphates. In assayed soil samples apatite was identified by x-ray analysis (Tatur and Barczuk 1984). In ten analyzed samples of excreta and minyulite free guano, the molar ratio of fluorine to calcium ranged from 0.15 to 0.43. After excluding one sample (H *in* Table 1) the range was from 0.15 to 0.26.

Table 1

Fluorine, phosphorus and calcium contents in excreta and guano of penguins and in ornithogenic phosphates from a phosphatized rock zone (% of dry weight)

Sample		F	P	Ca	Minyulite	Molar ratios	
Nr	Material	%	%	%	mm	F/P	F/Ca
E_1	Excreta	0.4466	—	—	—	—	—
E_2	,,	0.4228	—	—	—	—	—
E_3	,,	0.6886	—	—	—	—	—
E_4	,,	1.0280	3.21	9.6	0	0.52	0.26
E_5	,,	0.7428	2.73	6.0	0	0.44	0.26
G_1	Guano	1.0045	7.31	13.7	0	0.22	0.15
G_2	,,	1.0186	8.66	14.4	0	0.19	0.15
H	,,	2.2036	7.96	10.90	0	0.45	0.43
S	Phosphate	0.0039	12.44	0.41	0	0.00	0.02
L/M	,,	1.0125	9.31	4.80	21	0.18	0.44
L/X	,,	0.1111	7.32	0.19	9	0.02	1.23
M/X	,,	1.3025	7.59	0.85	74	0.28	3.23
M	,,	3.4500	13.76	0.55	233	0.41	13.23
A	,,	1.9606	11.19	1.50	0	0.28	2.76
T	,,	0.0990	17.84	0.10	0	0.01	2.09

Detailed description of the samples: fresh mixed excreta of: E_1 — *P. antarctica*, E_2 — *P. papua*; shells of krill from excreta of: E_3 — *P. adeliae*, E_4 — *P. adeliae* after long leaching in the field (coarse fraction), E_5 — sample E_4 fine fraction; G_1 — nitrogenous guano from the surface of the soil (coarse fraction > 1 mm diameter), G_2 — sample G_1 fine fraction < 1 mm, H — phosphatic guano from the soil subsurface, S — pure struvite from the soil surface, L/M — phosphatic clay with high content of leucophosphite and minyulite (from a phosphatized rock zone), L/X — phosphatic clay with high content of leucophosphite and undefined mineral with 8.9 A pattern (from a phosphatized rock zone), M — pure minyulite (hard, vesicular) from a phosphatized rock zone, A — almost pure amorphous aluminium phosphate, hard grains of gravel fraction (from a phosphatized rock zone), T — phosphatic clay of pure taranakite from a phosphatized rock zone.

Remarks: 1 — minyulite content was calculated on the base of 5.54 A x-ray pattern (height on difractogram *in* mm), 2 — samples of phosphates and the sample H were the same as in Tatur and Barczuk (1984). Phosphorus and calcium content and results of x-ray analysis were taken from this paper.

Therefore if all calcium was bound in apatite (which seems to be the case), it must be fluorapatite since the molar ratio of fluorine to calcium in this mineral $Ca_5(PO_4)_3(OH,F)$ is exactly 0.2.

The highest concentrations of fluorine (up to 3.2%) were found below a guano layer in the upper part of the phosphatized zone in the vicinity of large and old penguin rookeries. Minyulite was the main ornithogenic mineral in this soil horizon (profile 5 at depth 5—90 cm, profile 7 at depth 10—80 cm and probably profile 6 at depth 10—60 cm). A concentration of fluorine in pure minyulite (sample M *in* Table 1) equals 3,45% at F/P molar ratio 0.41. The molecular formula of this mineral was calculated on the basis of earlier analyses. (Tatur and Barczuk 1984) for $KAl_2\ (F_{0.82}OH_{0.18})\ (PO_4)_2\ 4H_2O$.

Concentrations of fluorine decreased sharply in the deepest layers, usually minyulite free (profile 6 at depth 60—150 m: Table 2) and in soils located off the rookery (profile 8 at depth 20—80 cm: Table 2). Concentrations of fluorine in these samples were very low, even when content of phosphorus was high (*see* molar ratio F/P).

Table 2

Fluorine, phosphorus and calcium concentrations in ornithogenic soils (% of dry weight)

Sample							Molar ratios	
Zone	Profile no.	Depth (cm)	F %	P %	Ca %	Minyulite mm	F/P	F/Ca
A	26	—10	0.4060	9.40	4.70	0	0.07	0.18
A	17a	0—3	1.3050	—	—	—	—	—
		10—20	0.7240	—	—	—	—	—
A	17	0—5	0.6090	7.44	5.70	0	0.13	0.26
		10—30	0.9180	6.30	8.50	0	0.24	0.23
B	5	2—15	1.4318	8.83	0.36	—	0.26	3.98
		15—45	2.8683	13.32	0.34	—	0.35	17.80
		45—70	3.0000	14.45	0.29	—	0.34	21.82
		70—90	2.4067	12.17	1.20	199	0.32	4.23
		90—95	1.6239	10.85	1.42	0	0.24	2.41
B	6	0—5	0.5800	6.85	5.90	0	0.14	0.21
		5—45	0.7650	7.20	0.20	—	0.17	8.07
		45—60	0.7255	8.32	0.12	—	0.15	12.75
		60—110	0.1860	5.15	0.24	—	0.06	1.63
		110—150	0.610	10.36	0.06	0	0.01	2.14
B	7	0—10	0.6460	5.68	2.70	67	0.19	0.50
		10—80	1.3700	8.58	0.85	—	0.26	3.40
B	8	3—20	0.3760	5.44	3.40	—	0.11	0.23
		20—80	0.0128	5.32	0.45	0	0.00	0.06
C	4	0—0.3	0.7795	7.00	8.00	0	0.18	0.21
		0.3—10	0.1600	4.38	2.90	—	0.06	0.12
C	3	0—10	0.0863	1.90	1.83	—	0.07	0.10
D	1	0—10	0.4605	4.86	4.80	—	0.16	0.20
		12—16	0.1330	1.44	3.50	—	0.15	0.08
		16—20	0.2510	3.68	4.40	—	0.11	0.12
E	15	0—10	0.0420	1.34	1.25	—	0.51	0.07
		below 10	0.0008	0.38	0.70	—	0.00	0.00

A — soils in the breeding rookery, B — soils in the zone with intensive deep phosphatization, C — soils in the zone of surficial accumulation of guano and phosphate at stony beaches, D — bottom sediments in the shallow pool below penguins rookery, E — soils in the zone of feathers accumulation on the soil surface.

Remarks: 1 — samples of the soil, phosphorus and calcium content are the same as *in* Tatur and Myrcha (1984), 2 — minyulite content was calculated on the base of 5.54 Å x-ray pattern.

Only in one minyulite and apatite free sample the concentration of fluorine was high (phosphatized zone — profile 5 at depth 90—95 cm). This sample was mainly composed of amorphous aluminium phosphate (sample A: Table 1). Such a high content of fluorine could be explained by a development of the molecular formula of this mineraloid AL_{10} $(F_{2.5}OH_{0.5})$ $(PO_4)_9$ about 43 H_2O (*cf.* Tatur and Barczuk 1984).

In ornithogenic soils of the penguin landing beaches (profile 4 at depth 0.3—10 cm and profile 3 at depth 0—10 cm) phosphates were relatively fluorine rich (F/P molar ratio about 0.07) in spite of a low absolute fluorine content (0.08—0.16%). This phenomenon was due to a dilution of phosphates with alluvial material. Both apatite and minyulite occurred there.

Fluorine content was low in soil samples from sites where penguins have moulted (profile 15 at depth 0—10 cm). The content of fluorine in the underlaying weathered volcanic rocks (profile 15 below 10 cm) was much below the average for this kind of material.

Statistical description of results

Concentration of fluorine in ornithogenic soils varied widely and was independent of ornithogenic phosphorus content (Table 3, also F/P molar ratio *in* Tables 1 and 2) as only two or three of six tested phosphates were fluorine bound. A distribution of fluorine in ornithogenic soils was controlled mainly by apatite and minyulite content and only exceptionally by amorphous aluminium phosphate.

Apatite bound fluorine in the surface guano layer due to neutral and alkaline reactions. Minyulite bound fluorine in a surface zone of phosphatized rocks where it was formed as a result of metasomatic reactions between acid guano leachates and weathered volcanic rocks. Zones of apatite and minyulite overlapped locally each other (sample L/X *in* Table 1, profile 7 at depth 0-10 cm *in* Table 2). A statistical analysis was used to evaluate the variability in fluorine content in connection with the apatite and minyulite content (Table 3). The mentioned samples containing aluminium phosphate (sample A *in* Table 1 and profile 5 at depth 90—95 cm *in* Table 2) were excluded from this calculation and will be described separately.

The obtained equation was significant for the both controlling factors. The varying content of apatite and minyulite explained 85% of changes in the fluorine concentration.

Table 3

Verification of factors (X_1, X_2, X_3) that control a fluorine concentration (Y) in ornithogenic soils

	X_1	X_2	X_3	
b_X	0.1001	0.0128	0.00787	
SE b	0.0208	0.0014	0.0271	
t	4.820	9.119	0.290	
P	<0.001	<0.001	>0.05	$R = 0.924$

Estimation of fluorine concentration (Y) occurring in connection with two significant factors (X_1, X_2) gives the following equation:

$Y = a + b_1X_1 + b_2X_2$
$R = 0.922 \quad n = 20$
$a = 0.0464$
$b_1 = 0.0984 \pm 0.0193 \quad t = 5.098 \quad P < 0.001$
$b_2 = 0.0129 \pm 0.00134 \quad t = 9.627 \quad P < 0.001$

where: Y — concentration of fluorine (%), X_1 — concentration of calcium (%) as a simplified value of apatite content, X_2 — high of 5.54 A x-ray pattern (mm), specific for the minyulite peak and can be used as a measure of its content, X_3 — concentration of phosphorus as simplified value of phosphate content (%).

Discussion

An occurrence of fluorine in calcium phosphate deposits has been noted by several authors, however this is the first description of a fluorine bound in minyulite and amorphous aluminium phosphate, formed during the ornithogenic phosphatization. Minyulite seems to be at least as important as apatite in ornithogenic soils of maritime Antarctic.

Earlier authors (Hutchinson 1950, White and Warin 1964, Altschuler 1973) reported enhanced fluorine content in ornithogenic deposits with calcium phosphates originated from a marine spray. Fluorine in ornithogenic (penguins) soils of the maritime Antarctic comes, however, mainly from krill, eaten by penguins. Tatur and Myrcha (1984) estimated that penguins deposited 10 kg dry excreta per a square metre a year in their breeding places. A concentration of fluorine in excreta was equal 0.43% (Table 1) and therefore the quantity of fluorine deposited in these areas amounts for 43 g per m^2/yr. If a sea water (with 1.3 mg/l) were the main source of fluorine (Warner 1971), then the amount of fluorine equal 43 g per m^2/yr, would have required 33 tons of sea water. This seems to be improbable because the greatest accumulations of fluorine were found 20 m above a sea level and at a distance of 100 m from the sea.

In krill fluorine was found mainly in shells (Adelung 1983, Buchholz 1983). They contain 0.26% of fluorine and are composed of chitin, protein and mineral compounds (after Keck 1983). A decomposition of the penguin excreta containing disintegrated krill remains leads to a concentration of shells with weathered chitin and scattered aggregates of calcium phosphate inside and on the surface of the organic structure (Pietr, Tatur and Myrcha 1983). Calcium phosphate was determined with x-ray analysis as apatite, probably hydroxylapatite (Tatur and Barczuk 1984). Results of this paper find it however to be fluorapatite. Concentrations of calcium and fluorine during a decomposition of excreta and guano changed simultaneously with the constant molar ratio of F/C close to apatite one (about 0.2), at the excess of phosphorus. An occurrence of fluorapatite in guano could have resulted therefore from simple releasing and recrystallization of previously amorphous calcium phosphate (Posner, Blumenthal and Betts 1984) during a mineralization of the organic matter in the excreta. Fluorapatite is unstable in soil and may be easily dissolved by periodic acid guano leachates (Brown 1973, Tatur and Myrcha 1983). A dissolution must be rapid because of microcrystalline structure (Tatur and Barczuk 1984) and a large specific surface of this mineral (Posner, Blumenthal and Betts 1984).

Fluoride ions released during the dissolution of fluorapatite percolate through the soil in an acid solution and may be bound again in the subsurface layer of a soil with potassium aluminium phosphate *i.e.* minyulite (Tatur and Barczuk 1984). Minyulite forms due to a metasomatic phosphatization of silicates what requires a high much phosphorus and alkalis as well as fluorine. The existence of fluorine free minyulite is inlikely (Spencer, Bannister and Hey 1943, Haseman, Lehr and Smith 1950. Tatur and Barczuk 1984). Thus, minyulite may be probably formed only syngeneticly during manuring in contrast to fluorapatite. However, fluorapatite may be also formed later by an isomorphous subsitution of OH by F in the earlier, syngeneticly formed hydroxylapatite.

Minyulite is also unstable and requires a high ion concentration in soil solutions, therefore its occurrence depends on a permanent manuring by birds. When the manuring stops, rain and melt water dissolves this mineral, leaving simply aluminium phosphate while releasing potassium and some phosphorus into the solution (Cole and Jackson 1950, Taylor and Gurney 1961).

In the assayed soils a natural paragenesis of minyulite plus amorphous aluminium phosphate occurred (sample M and A *in* Table 1), described in details earlier by Tatur and Myrcha (1984). The phosphatic soil (profile 5 *in* Table 2) composed almost of pure minyulite (sample M *in* Table 1), forms a layer 95 cm thick. A bottom of this profile occurs below a ground water level (profile 5 at depth 90—95: Table 2) and amorphous aluminium phosphate was the main mineraloid of this layer (sample A *in* Table 1), containing still plenty of fluorine. The deepest layer of this soil profile was under alternate leaching by solutions of various chemical compositions: 1) supersaturated solutions coming from the rookery and percolating through this soil, 2) pure ground water coming from the catchment area laying above the penguin rookeries.

An incongruently dissolving of minyulite to the amorphous aluminium phosphate with releasing of potassium at the bottom of the profile appeared during washing out of the soil by a pure ground water while supersaturated guano leachates supplied the excess of fluorine bound by this mineraloid. Described distribution of fluorine in the alteration process of minyulite was found only in a single place and therefore it can be considered as the local one.

The course of chemical degradation of fluorine bearing ornithogenic phosphates is now better understood, although the rate of this process (and return of fluorine to the sea) is difficult to estimate. The ornithogenic fluorine deposits may be regarded as the geologicly unstable features in the climatic conditions of maritime Antarctic.

Acknowledgements. I am grateful to A. Keck, B. Culik and the leader of the team Professor D. Adelung for carrying out a determination of fluorine and to Professor S. Rakusa-Suszczewski for contacts. I thank also W. Trivelpiece and S. Trivelpiece for reviewing the manuscript.

References

Adelung D. 1983 — Zur Bedeutung des Fluors im antarktischen Ökosystem — Berichte zur Polarforschung 10: 10—15.

Altschuler Z. S. 1973 — The weathering of phosphate deposits — geochemical and environmental aspects (In: Environmental Phosphorus Handbook, Eds. E. J. Griffith, A. Beeton, J. M. Spencer, D. T. Mitchell) — J. Wiley and Sons, New York, London, Sydney, Toronto, 33—96.

Brown W. E. 1973 — Solubilities of phosphates and other springly soluble components (In: Environmental Phosphorus Handbook, Eds. E. J. Griffith, J. M. Spencer, A. Beeton and D. T. Mitchell) — J. Wiley and Sons, New York, London, Sydney, Toronto, 203—263.

Buchholz F. 1983 — Die Dynamik des Fluoridegehaltes im Häutung szyklus der Euphausiiden —Berichte zur Polarforschung 10: 34—45.

Cole C. V., Jackson M. L. 1950 — Solubility equilibrium constans of dihydroxy — aluminum dihydrogen phosphate relating to a mechanism of phosphate fixation in soils — Soil Sci, Soc. Am. 84—89.

Emigh G. D. 1973 — Economic phosphate deposits (In: Environmental Phosphorus Handbook, Eds. E. J. Griffith, A. Beeton, J. M. Spencer and D. T. Mitchell) — J. Wiley and Sons, New York, London, Sydney, Toronto, 97—116.

Haseman J. F., Lehr J. R., Smith J. P. 1950 — Mineralogical character of some iron and aluminum phosphates, containing potassium and ammonium — Soil Sci. Soc. Am. Proc. 15: 76—84.

Hutchinson G. E. 1950 — Biogeochemistry of vertebrate excretion — Bull. Amer. Mus. Nat. Hist. 96: 1—554.

Keck A. 1983 — Fluorid in Meerestieren und Fragen zur Fluoridakkumulation im krill — Berichte zur Polarforschung 10: 41—45.

Pietr S., Tatur A., Myrcha A. 1983 — Mineralization of penguin excrements in the Admiralty Bay region (King George Island, South Shetland Islands, Antarctica) — Pol. Polar Res. 4: 97—112.

Posner A. S., Blumenthal N. C. and Betts F. 1984 — Chemistry and structure of precipitated hydroxyapatites (In: Phosphate Minerals, Eds. J. O. Nriagu, P. B. Moore) — Springer-Verlag Berlin Heidelberg, New York, Tokyo, 330—350.

Spencer L. J., Bannister F. A., Hey M. M. and Bennet H. 1943 — Minyulite/hydrous K-Al fluorphosphate from South Australia — Mineral. Mag. 26: 309—314.

Tatur A., Barczuk A. 1984 — Phosphates of ornithogenic soils on the volcanic King George Island (maritime Antarctic) — Pol. Polar Res. 5: 61—97.

Tatur A., Myrcha A. 1983 — Changes of chemical composition of waters running off from penguin rookeries on King George Island (maritime Antarctic) — Pol. Polar Res. 4: 113—128.

Tatur A., Myrcha A. 1984 — Ornithogenic soils on King George Island, South Shetland Islands (maritime Antarctic Zone) — Pol. Polar Res. 5: 31—60.

Taylor A. W., Gurney E. L. 1961 — Solubilities of potassium and ammonia taranakites — J. Phys. Chem. 56: 1613—1616.

Volkman N. J., Presler P., Trivelpiece W. 1980 — Diets of pygoscelid penguins at King George Island, Antarctica — Condor 82: 373—378.

Warner T. B. 1971 — Normal content of sea water — Deep Sea Res. 18: 1255—1263.

White W. C., Warin O. N. 1964 — A survey of phosphate deposits in the Southwest Pacific and Australian Waters — Bureau Min. Res. Aust. Bull. 69: 173 pp.

Received September 22, 1986
Revised October 21, 1986

Резюме

Проведены определения флуора в минералах (Таб. 1) и орнитогенных почвах (Таб. 2), образующихся вокруг мест гнездования и лежбищ пингвинов из видов *P. antarctica* и *P. adeliae* на острове Кинг Джордж в районе залива Адмиралти.

Было установлено высокое содерманит флуора в исследуемых почвах. Флуор выносится из моря на берег пингвинами. Они питаются крилем, который богат этим элементом (0,11%). Содержание флуора повышается в фекалиях этих птиц, выделянных вблизи мест гнездования (до ок. 0,43%), а после разложения и промывки фекалий до 1,03%. После дальнейшего разложения органической материи наблюдается дальнейший рост концентрации флуора в слое гуана (до 2,2%). Флуор накапливается также в приповерхностной зоне фосфатизированных скал, находящейся вблизи больших и многочисленных колоний (до 3,4%).

Было доказано, что в орнитогенных почвах распределение флуора зависит прежде всего от распределения двух фосфатов, связывающих флуор: апатита и минулита, при чем соотношение содержания флуора и содержанию фосфора (соотношение F/P — Таб. 1 и 2) не столь близко, поскольку в исследуемых почвах широко выступают другие фосфаты, которые не содержат флуора. Представленный вывод поддерживается регрессионным уравнением (Таб. 3).

Апатит, образующийся из минерализирующегося органического вещества, связывает флуор в поверхностном слое почвы в условиях нейтральной и щелочной реакции. Флуор уволняется из апатита во время циклического подкисления этих почв, в результате

чего апатит растворяется. Флуор, проникающий вглубь почвы в кислых растворах, может связываться в низлежащем слое фосфатизированных скал в гидратированном алюмини — калийном фосфате — минулите.

Минулит образуется в результате метасоматических реакций между кислыми обмывками гуана и дресвой (выветрелостью) вулканических скал типа андезита и базальта. Следует ожидать что произойдет инконгруэнтное растворение этого минерала, когда только в почву перестанут поступать минеральные удобрения -з фекалий пингвинов и почвы будут промыватся слабо минерализованными водами из осадков и таящих снегов. Продуктом этого процесса является простой аморфный фосфат алюминия, калий же и флуор переходят в раствор. Однако, в определенных ситуациях флуор, в орличие от калия, может тоже задерживаться в аморфном фосфате алюминия.

Streszczenie

Przeprowadzono oznaczenia fluoru w minerałach (tab. 1) i glebach ornitogennych (tab. 2) tworzących się wokół miejsc lęgowych pingwinów z gatunku *P. antarctica* i *P. adeliae* na Wyspie Króla Jerzego w rejonie Zatoki Admiralicji.

Stwierdzono wysokie zawartości fluoru w badanych glebach. Fluor wynoszony jest z morza na ląd przez pingwiny. Odżywiają się one zasobnym w ten pierwiastek krylem (0,11%). Zawartość fluoru wzrasta w odchodach tych ptaków wydalanych na obszarze miejsc lęgowych (do około 0,43%), a po rozkładzie i przemyciu odchodów do 1,03%. Po dalszym rozkładzie materii organicznej następuje dalsza koncentracja fluoru w warstwie guana (do 2,2%). Fluor akumulowany jest również w powierzchniowej strefie sfosfatyzowanych skał przylegającej do dużych i liczebnych kolonii (do 3,45%).

Udowodniono, że rozmieszczenie fluoru w glebach ornitogennych uzależnione jest przede wszystkim od rozmieszczenia w nich dwóch wiążących fluor fosforanów: apatytu i minyulitu, przy czym związek zawartości fluoru z zawartością fosforu (stosunek F/P: tab. 1—2) jest dość luźny, gdyż w badanych glebach powszechne są też inne fosforany nie zawierające fluoru. Powyższy wniosek udokumentowano równaniem regresji (tab. 3).

Apatyt powstający z mineralizującej się materii organicznej wiąże fluor w powierzchniowej warstwie gleby w warunkach odczynu obojętnego i alkalicznego. Fluor uwolniony zostaje z apatytu w wyniku cyklicznie występujących okresów zakwaszania tych gleb, podczas których apatyt zostaje rozpuszczony. Fluor przesiąkający w głąb gleby w kwaśnych roztworach, może zostać związany w podległej warstwie sfosfatyzowanych skał w uwodnionym fosforanie glinowo potasowym — minyulicie.

Minyulit powstaje w wyniku reakcji metasomatycznych między zakwaszonymi popłuczkami guana a zwietrzeliną skał wulkanicznych typu andezyt i bazalt. Należy oczekiwać inkongruentnego rozpuszczania tego minerału, gdy tylko nawożenie organiczne przez pingwiny zostanie przerwane i gleby przemywane będą słabo zmineralizowanymi wodami opadowymi i roztopowymi. Produktem tego procesu jest prosty amorficzny fosforan glinu, natomiast potas i fluor przechodzą do roztworu. W pewnych jednak sytuacjach fluor w odróżnieniu od potasu może być zatrzymany również w amorficznym fosforanie glinu.