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## **BIOGENIC PHOSPHATE AND SULPHATE MINERALS IN THE SOILS OF ANTARCTIC PENINSULA**

### **INTRODUCTION**

Phosphatization caused by bird manuring and weathering processes of sulphide-bearing sediments, are the examples of mineralization in Antarctic soils constrained by microbiological activity. The final result of both processes is clear, since they proceed in the environment undisturbed by the other natural processes occurring usually elsewhere in the background. Biogenic phosphates has not been described in Antarctica yet, except of one paper (Wilson and Bain 1976), in spite of numerous papers dealing with ornithogenic soils (Campbell and Claridge 1987). Both associations of minerals are durable in given conditions: phosphatization needs liquid water in soils, whereas sulphates required rather dry conditions. Therefore, phosphates occur exclusively in maritime, but sulphate were found till now only in continental climatic conditions.

### **SAMPLES AND METHODS**

The samples for the present study, collected during many seasons of field works, came from King George Island and Seymour Island located near the Antarctic Peninsula. Usually soft “clay” accumulations of diversified minerals were taken for studies. The term “clay” means traditionally in such case only grain size class. Chemical analysis of pre-concentrated samples has been conducted in the Institute of Ecology, Polish Academy of Sciences. AAS and spectrophotometric methods were applied. Chemical formulae of particular minerals have been calculated from almost pure accumulation of minerals. Petrological and mineralogical studies have been performed in the Institute of Mineralogy, Geochemistry and Petrology, Faculty of Geology, Warsaw University. Observations using scanning and petrographic microscopes and energy dispersive X-ray microanalyses were performed. X-ray diffraction pattern was used for mineral identification, thermal analyses (DTA, DTG, TG), infrared spectroscopy, microscopic observations and chemical analysis supported determinations.

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## RESULTS

Ornithogenic soils in the maritime Antarctic (western side of the Antarctic Peninsula) consist of surface guano layer and phosphatization zone underneath, which has been formed due to action of aggressive, often supersaturated guano leachates on the bedrock. The main feature of microbiological phosphatization is a changeable reaction of solution percolating through the ornithogenic soil, which is controlled by microbiological processes of organic matter decomposition and transformations of mineral nitrogen forms in soil (ammonification producing alkaline ammonia ions followed, or not, by nitrification producing acid nitrates). Association of minerals is then modified by periodic washing of soils by melt-water, that led to chemical degradation of phosphates by incongruent dissolving and excretion of new, more simple phases. Phosphatization in extreme case may lead to total removing of host silicates, which are replaced by phosphates (Tatur et al. 1993). The following phosphate minerals form ornithogenic soils in the humid climate of maritime Antarctic (Tatur, Barczuk 1985; Tatur 2002):

**Minerals in the guano layer:** urates –  $(\text{NH}_4 \gg \text{K, Na})_{0,8}(\text{Mg, Ca, Fe})_{0,1}\text{C}_5\text{H}_3\text{O}_3\text{N}_4$ ; struvite –  $\text{Mg}(\text{NH}_4)\text{PO}_4 \times 6\text{H}_2\text{O}$ ; fluorapatite –  $\text{Ca}_5(\text{PO})_4\text{F}$ ; hydroxyapatite  $\text{Ca}_5(\text{PO})_4\text{OH}$ ; brushite –  $\text{Ca}(\text{HPO})_4 \times 2\text{H}_2\text{O}$ .

**Minerals in the phosphatized zone:** leucophosphite –  $(\text{NH}_4, \text{K})_2(\text{Fe, Al})_4(\text{PO}_4)_4(\text{OH, F})_2 \times 4\text{H}_2\text{O}$ ; minyulite –  $\text{KAl}_2(\text{F, OH})(\text{PO}_4)_2 \times 4\text{H}_2\text{O}$ ; taranakite –  $(\text{K, NH}_4)_3\text{Al}_5\text{H}_6(\text{PO}_4)_8 \times 18\text{H}_2\text{O}$ ; highly hydrated, basic, amorphous aluminium phosphate bearing fluorine up to –  $\text{Al}_{10}\text{F}_9(\text{PO}_4) \times n\text{H}_2\text{O}$ .

**Minerals found exclusively in phosphatized zone of relic soils in abandoned penguin rookeries:** vashegyite A –  $(\text{Al}_{0,9}\text{F}_{0,1})(\text{PO}_4) \times 3,15\text{H}_2\text{O}$ ; vashegyite B –  $\text{Al}_{11}(\text{OH, F})_3(\text{PO}_4) \times 3,15\text{H}_2\text{O}$ ; “arctowskite” –  $(\text{Al}_{8,4}\text{Fe}_{0,6})_9(\text{OH})_3(\text{PO}_4)_8 \times 27\text{H}_2\text{O}$ .

**Phosphates from the surrounding areas:** vivianite –  $\text{Fe}_3(\text{PO}_4)_2 \times 8\text{H}_2\text{O}$ .

Oxidation of sulphides mediated by soil bacteria led to the formation of strongly acid solutions bearing sulphuric acid, which reacts with carbonates and silicates from the bedrock. Results of this acid sulphate drainage were observed on Seymour Island (eastern side of Antarctic Peninsula), with dry continental climate protecting against easy dissolving of sulphates. The following simple salts were found in the weathering zone of Tertiary sand interbedded with sulphide-bearing clay and containing carbonates concretions and dispersed shell hash:

**K-Na jarosite** is an important component of yellow clay occurring commonly in the weathering zone where it forms lenses, striae, and irregular patches, especially at the contacts with layers of bituminous clay bearing sulphides. Na jarosite can be often found near the shoreline, whereas K jarosite rather in the inland sites.

**Gypsum**, a common minor mineral in the weathering zone, wherever common carbonates occur. It forms crusts on bottom sides of carbonate boulders, indurated calcic horizons, minute desert roses dispersed in the loose sand, surface encrustations, lamination inside hard lithified ferrihydrite banks.

**Basic Ca-bearing aluminium sulphate**, amorphous to X-ray. It occasionally forms white soft clay covering carbonate concretions as the result of its reaction with acid sulphate solutions bearing Al.

**Ankerite** forms crusts on calcium carbonate concretions originated due to action of iron <sup>2+</sup> rich acid solutions on carbonates.

**Ferrihydrite sometimes rich in Al** is together with gypsum the main component of cement in the common thick, erosion-resistant, brown coloured banks of lithified sand. This mineral is also the component of illuvial-type soil horizons and stains the upper side of stones laying on the soil surface. It may be considered as the final stable stage of the surface iron mineralization.

Ephemeral, minute yellow-to-white efflorescences, observed sometimes on the soil surface and obtained during evaporation of soil aqueous solutions in laboratory, were identified as a mixture of well crystallized water soluble **natrosiderite**, **hexahydrite**, **tamarugite**.

Cretaceous silty sands of Seymour Island do not contain sulphides and yielded only a simple mineralization on the bottom and upper surfaces of basaltic stones laying on the soil surface (stones are derived from nearby dykes).

**Aragonite** forms crusts on the underside of cobbles always drowned in the soil, green colouration comes from admixture of chlorite pigment.

**Ferrihydrite** forms reddish-brown staining on the upper side of the same cobbles. During dry periods a white superficial cover of **halite** occurs everywhere.

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