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REDAKTOR IVAN KLÁŠTERSKÝ

KAREL KOMÁREK:

VÝKVĚTY NA SLATINĚ U PODĚBRAD.

EFFLORESCENCES IN THE LOWLAND MOORS NEAR PODĚBRADY.

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KAREL KOMÁREK:

Výkvěty na slatině u Poděbrad.
Efflorescences i the Lowland Moors near Poděbrady.

(Předloženo 15. VII. 1950.)

Poděbrady a jejich okolí jsou s hlediska mineralogického velmi chudé. Čtvrtohorní nánosy hlíny nebo písku jsou navrstveny přímo na opukách křídového útvaru. Ani labský písek vytěžený čerstvě bagrováním neobsahuje žádný pozoruhodný nerost, nýbrž toliko malé oblázky většinou jen zcela obecných odrůd křemene nebo valounky hornin, přinesených sem z horního toku Labe. Jedině v době kolem první světové války když bylo vyhlubováno pro Labe nové řečiště, bylo možné nalézt v místech regulace i poměrně velké kusy *chalcedonů* nebo *achátů* a v čerstvě nalámané opuce nebo v jílu zase drobné krystalky *pyritu* a *markasitu*. O tom však v literatuře nikde není dosud žádná zmínka. Proto také J. KRATOCHVÍL ve svém monumentálním díle (1) uvádí z Poděbrad jen jediný nerost a to *mira-bilit*, který tam byl prý kdysi nalezen na mokřínách, podle zprávy F. SITENSKÉHO. Skutečně SITENSKÝ ve svém obšírném spise (2) zmiňuje se o uvedeném nálezu, ač jen letmo, jedinou stručnou větou: „In eisenkies- und kochsalzhaltigen Mooren (wie z. B. in jenen bei Franzensbad, Seestadt, Oužic, Poděbrad) entsteht im Torfe Glaubersalz.“ SITENSKÝ se zajímal jen o rašeliny a bělavé výkvěty, které v okolí Poděbrad před více než půlstoletím na slatinách našel, považoval bezpochyby bez jakéhokoliv bližšího výzkumu za vyloučený síran sodný. Od té doby však skoro všechny polabské slatiny zanikly, k čemuž přispěla hlavně regulace labského toku, prováděná v době kolem první světové války. Dnes bychom marně po nich pátrali, neboť byly přeměněny v louky nebo pole. Není však dosti dobře pochopitelné, proč výkvěty na slatinách, vznikajících tehdy většinou na starých labských ramenech, podle zprávy SITENSKÉHO měly být tvořeny zrovna jen síranem sodným, když ani v labské vodě (3) ani v půdě není v těch místech sodík nijak zvlášť rozšířen. Proto nálež SITENSKÉHO se mi zdál málo pravděpodobným. Přesné rozřešení otázky se dá provést jen podrobnějším výzkumem výkvětů a to jak mineralogickým tak zejména i che-

mickým. K tomu lze však z celého širého okolí Poděbrad použít dnes toliko jediné lokality, neboť nikde jinde se již slatina nevyskytuje. Je to slatiště na jihozápad od města, k němuž se dostaneme, jestliže se státní silnice cestou od hřbitova (směrem od Prahy) sejdeme vlevo vozovou cestou, vedoucí do lesa Obory. Slatinná hmota tam tvoří podloží rozsáhlé louky, rozprostírající se od Obory směrem ke hřbitovu. Ložisko slatiny bylo tam objeveno v roce 1921 a hned již v příštím roce byly zavedeny v poděbradském léčebném ústavu rašelinové koupele, při nichž se nově nalezené slatiny začalo používat k léčení. Od té doby se v oněch místech slatinná hmota k léčebným účelům těží každoročně a nechává se pak delší dobu ještě na místě nakupena v hromadách, aby zvětrala. Po vytěžené slatině zůstávají do dnešní doby dva rybníčky, jejichž charakter po stránce faunistické a floristické jsem v nejhrubších obrysech stanovil.

Hojné bílé výkvěty jsem našel na hromadě vytěžené slatinné hmoty, ležící mezi větším rybníčkem a vozovou cestou, vedoucí do Obory. Slatina není těžena v borkách, nýbrž je píchána v nepravidelných kusech, na jejichž spodní a boční straně se vytvářejí bělavé výkvěty pozvolným odpařováním roztoků, prosakujících po dešti hmotou slatiny. Výkvěty jsou práškovité a jen na zetlelých listech vodních rostlin nebo i na kusech větví, v slatinné hmotě se vyskytujících tvoří jemné, toliko až 2 mm dlouhé, jehličkovité krystalky, o nichž jsem mikroskopickým i chemickým výzkumem dokázal, že to jsou drobné krystalky *s á d r o v c e*. Přes to bylo chemicky zkoumáno ještě složení výluhu, získaného z bělavé hmoty výkvětu studenou vodou. Alkalické kovy byly tam nalezeny jen ve zcela nepatrném množství. Také byla chemicky zkoumána voda obou rybníčků, vyznačující se jak vysokým obsahem vápníku, tak i značnou tvrdostí uhličitanovou i množstvím síranů. Byla odvozena i hlavní chemická reakce, kterou se ve slatině vytvořil sádrovec spolu s limonitem.

Z provedených prací vysvítá, že výkvět na slatině u Poděbrad se skládá téměř z čisté sádrovce a že ani v dřívějších dobách nebyly na slatinách u Poděbrad podmínky pro tvorbu mirabilitu, nýbrž, že tehdejší výkvěty na mokřinách třeba přičísti též jen *s á d r o v c i*.

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No remarkable minerals occur in the Quaternary deposits near Poděbrady, nor do such minerals occur in the sands of the Elbe. J. KRATOCHVÍL in his large work on Bohemian minerals (1) mentions only one mineral from the neighbourhood of Poděbrady which is also mentioned in literature. This mineral was found by F. SITENSKÝ (2) who mentions only briefly and incidentally that Glauber's salt is still being formed in the lowland moors near Poděbrady and elsewhere. SITENSKÝ was interested only in the peats and as for the whitish efflorescences which he found in the lowland moors in the neighbourhood of Poděbrady more than half a century ago he considered them obviously, without any closer examination, as sodium sulphate. Since then, however, almost all lowland moors of the Elbe region have disappeared, mainly as the result of the regulation of the Elbe which was carried out at about the time of World War I. Today we look in vain for these moors, as they have been turned into meadows or fields. The lowland moors of the Elbe region arose

formerly mostly in old river channels of the Elbe, but the regulation of the river completely drained these channels and turned them into meadows. It is, however, puzzling why the efflorescences on the lowland moors near Poděbrady should be formed just by sodium sulphate, as sodium is not specially abundant in these places either in the water of the Elbe or in the soil. According to the analysis of the water of the Elbe at Čelákovice, made at the time (1892) by J. HANAMANN (3), 1 liter of water contained only 0,01178 gr. Na_2O , but at the same time 0,08202 gr. CaO , which yields the figure of 0,00874 gr. for Na and 0,05862 gr. for Ca. Taking in consideration that sodium sulphate is at 18° C about 44 times more soluble in water than calcium sulphate it is clear that no explanation can be found for its separating out from its aqueous solutions, especially from such in which there is nearly seven times more calcium. Thus SITENSKÝ's finding seems but little trustworthy to me. An accurate and correct solution of the question can be obtained only by a detailed mineralogical and especially also chemical investigation of the efflorescences. For this purpose, however, only one locality can be used today in the whole of the farther environment of Poděbrady, as the bottom peat is not exposed anywhere else at present. This locality is the lowland moor southwest of the town of Poděbrady, reached by going down from the main road from the cemetery (in the direction from Prague) to the left by the carriage way leading to the wood Obora. The lowland moor forms here the substratum of a large meadow stretching from the Obora in the direction towards the cemetery. Here a deposit of bottom peat was discovered in 1921, and already the following year mud baths were introduced in the Poděbrady health establishment, utilizing the newly discovered bottom peat for treatment. Since then the bottom peat has been exploited every year in these places for therapeutic purposes, usually only after the main spa season is over at the end of summer or also in early autumn. It is cut in irregular pieces, which are left for a rather long time heaped together, while a weathering of some of their components takes place. Two small ponds have remained where the bottom peat was taken out; they stretch parallel to the carriage way, at about 15 m. from it, behind a row of high alders.

The older pond, situated more to the north, is the larger one (45×27 m.) and with regard to the fauna and flora richer than the second pond. Its north and east shores are irregular, covered with different kinds of sedge (*Carex*), also burweed (*Sparganium*) occurs here. In July 1950 I flushed here in the noon hours a little bittern (*Ixobrychus minutus*), an adult male, though near-by were flocks of domestic geese and ducks. In several places the water-plantain (*Alisma plantago*) grows out of the water. The Canadian water weed (*Elodea canadensis*) formerly very abundant here has receded in more recent times, and the water milfoil (*Myriophyllum spicatum*) spreads here unusually strongly. Hornwort (*Ceratophyllum demersum*) is abundant, at the eastern shore the water crowfoot (*Batrachium divaricatum*); at the shore in these places also rushes (*Juncus conglomeratus*) grow in a cover of slough grass. Fish coming here during the spring floods multiply strongly. In the summer one can see large flocks of fish-fry in addition to sporadic adult pikes, tenches and other cyprinoidean fishes, whose length however but rarely

exceeds 30 cm. *Crayfish* can also be found in the hollows of the concave bank. The domestic ducks and geese destroy the vegetation here considerably and hunt especially tadpoles. In many places the water is permanently made muddy by them. Sometimes it is possible to surprise here a *musk-rat* or *adders*. Abundant white efflorescences were formed on the bottom peat taken from here during its lying in heaps; the investigation of these efflorescences will be dealt with in another paper. The bottom peat contains here mainly only moss and remains of aquatic plants, but only relatively little wood and branches of trees.

The smaller pond (22,5×29 m.), situated more to the south, was formed only in the last years by peat-cutting. At its southern margin, from where the ground rises already in the direction towards the main road, the deposit of bottom peat has just been exhausted, and passes into clay and sand. The surface of the pond is covered with duck-weed (*Lemna*). Recently the pond has become much overgrown with the Canadian water weed (*Elodea canadensis*). The bottom peat cut here contains very abundant remains of wood, mostly quite soft, often fragments of trunks even more than 20 cm. thick, but relatively only few remains of moss. I gave samples of the woods found in this bottom peat to Dr. I. KLÁŠTERSKÝ for the Botanical Department of the National Museum as documentary material and for investigation. The whitish efflorescences on this bottom peat were few, also when it had lain many months in heaps. Some pieces of bottom peat remained black after drying out, others assumed a much lighter, brown-gray coloration. Also many clay vessels of ancient cultures were found in this lowland moor.

Reed grass (*Phragmites communis*) and sweet-flag (*Acorus calamus*) lack completely in both ponds, though they are common on the Elbe. The two ponds are separated by a common dyke (27 m.), but at the time when the water is high they are connected by a narrow and shallow canal left in the middle of the dyke. On the dyke are found the tubes of the pumping plant, by means of which an electric motor carries out the draining before one begins to cut the bottom peat.

For the *microscopic* and *chemical* investigation I used the white efflorescences which appeared in abundant quantity at the end of 1949 on a heap of bottom-peat situated north of the larger pond. The efflorescences were most abundant on the lower and lateral sides of the pieces of bottom-peat, as they were indubitably formed here by the gradual evaporation of solutions that had infiltrated the bottom-peat after rain in a vertical direction downwards. The efflorescences had the appearance of a white powder, which under magnification under the microscope appeared as irregular heaps of a white substance without any crystal appearance. But on rotten leaves or root-stocks of large water-plants, also on fragments of branches or wood occurring in the bottom peat, it was possible to observe fine acicular needles (crystals), only about 2 mm. long. For purposes of investigation a greater number of these needles was carefully detached and assembled in a flat dish.

In the *microscopic investigation* it was found that the acicular crystals have the shape of ordinary flat rulers and end obliquely. In the polarization microscope between crossed Nicols the needles

show a distinctly inclined extinction of 37° — 38° and 52° — 53° . Already from this optical investigation we can infer with the greatest probability that the mineral investigated is gypsum. But for making a true identification it was nevertheless necessary to make still also some chemical tests.

As the fine crystal needles of the examined substance occurred only in a small quantity on the bare remains of rotten leaves, I used for their *chemical investigation* microchemical methods. As gypsum itself is the chief compound formed in the microchemical detection of *calcium* and *sulphates* it was necessary to carry out other reactions. A rather large number of laboriously separated acicular crystals was mixed in a small conical test tube with several drops of distilled water, and the suspension obtained was stirred with a thin glass rod for a fairly long time in order to ensure that a saturated solution was formed. After centrifugation the clear supernatant liquid was separated by means of a pipette from the solid at the bottom of the centrifugal cone, which could not be dissolved, and it was then used to make the general preliminary tests as well as tests for *calcium* and *sulphates*. The reactions were made by using current microchemical techniques, always only with part of one drop of the solution, upon an object slide placed once on white and once on black paper, so that by the contrast formed it might be possible to ascertain the expected reaction even if it took place only to a slight extent.

To the saturated aqueous solution obtained from the needles in the manner just described was added some freshly prepared saturated water solution of *hydrogen sulphide*. No precipitate nor any coloration was observed, not even when the object slide with the reaction solution was inverted for a fairly long time over a dish with concentrated ammonium hydroxide. Thus the absence of heavy metals was proved. *Silver nitrate* was added to another part of the solution. No precipitate was formed. Some saturated solution of *ammonium oxalate* was added with a glass rod to a further part of the solution. A white precipitate of calcium oxalate was formed immediately, which disappeared after the addition of diluted sulphuric acid but reappeared after inversion of the object slide over a dish with concentrated ammonium hydroxide. Some solution of *barium nitrate* was added to another part of the solution. A white precipitate appeared immediately, insoluble in nitric acid, formed by barium sulphate. These tests thus established clearly that the substance of the small acicular needles occurring not too abundantly on the bare surface of rotten remains of leaves in the bottom peat is formed by calcium sulphate. Thus also the earlier microscopic finding was simultaneously confirmed.

But this investigation had shown nothing definite about the main substance of the white efflorescent crust, which, under microscopical magnification, did not show any crystal form, and which covered in a dense layer the lower and lateral sides of the pieces of bottom peat. It was not possible to separate the efflorescence completely from its base, for even when wiped off carefully brown particles of the substratum projecting a little more from the bottom peat were loosened. The efflorescence forming on the surface of the pieces of bottom peat was, judging from its position, evidently formed only by substances

soluble already in cold water (in rain). Thus attention had to be paid especially to the extract obtained from the superficial bottom peat rich in efflorescence only by mere *cold distilled water*. The total chemical composition of the bottom peat of Poděbrady is well known, for W. BENADE, then Director of the Institute of Peat Investigation at Františkovy Lázně, had himself carried out its model chemical analysis in spring 1943. This analysis had not been published separately, but F. LENOCH (4) reports it in his discussion with A. MLÁDEK on the manner of preparation of mud baths. According to BENADE's analysis the bottom peat of Poděbrady dried at 105° C contains in addition to other compounds also 2.31% Fe₂O₃, 3.39% CaO, 0.69% MgO, 0.52% K₂O, 0.73% Na₂O, and 1.58% SO₃. By conversion into metals or ions we get the following results: 1.62% Fe, 2.42% Ca, 0.42% Mg, 0.43% K, 0.54% Na, and 1.90% SO₄". But for the chemical investigation of the efflorescence I had to take into account only that part of the bottom peat which is soluble already in cold water. Thus it was necessary first to make a *qualitative analysis* of the aqueous extract. 80 gr. of powdered substance scraped from the surface of the pieces of bottom peat in places where there was sufficient white efflorescence was extracted by using a total of 300 ml. of cold distilled water in several portions. A filtrate only quite slightly yellowish was obtained, which was evaporated in a platinum dish to dryness, dried at 180° C (when gypsum already loses its water of crystallization), and weighed. Thus I obtained a total of only 0.59 gr. of residue coloured brown. To the dried residue was added distilled water and after fairly long stirring with a glass rod an entirely clear solution was obtained which was filtered into a 250 ml. graduated flask. No visible insoluble residue remained, so that the filtration was unnecessary. The solution was diluted with water up to the graduation mark and the slightly yellowish brown solution was thoroughly mixed. A qualitative analysis was made with a small portion of the solution obtained. Before searching for heavy metals an ashing was carried out by evaporating the solution finally with concentrated sulphuric acid in order to decompose the humic matters and other organic compounds so that they could not fix the heavy metals in complexes stable against the reagents used in the further analysis.

By the qualitative analysis systematically carried out it was found that the aqueous extract from the efflorescence obtained in cold water contains of metals only a great amount of *calcium*, some *magnesium*, a small amount of alkali metals, and traces of *manganese* (BENADE does not mention Mn). The *iron* does not pass into this extract. Of anions were found mainly only *sulphates*, whereas *chlorides* and *phosphates* were found only in small quantities.

In the *quantitative analysis* of the extract obtained by extraction of the efflorescence with cold water the *calcium* was determined after precipitation as calcium oxalate by titration with permanganate. The *magnesium* was precipitated in the remaining filtrate as magnesium ammonium phosphate, which was converted by ignition into magnesium pyrophosphate and weighed. *Sodium* and *potassium* were determined together polarographically in another portion of the solution by using

a freshly prepared solution of tetramethyl ammonium hydroxide, to which was added some pure phosphoric acid (5). The *sulphates* were determined by precipitation as barium sulphate. According to calculation the total amount (0.59 gr.) of solid was found to be: 0.1120 gr. Ca which would correspond to 0.3804 gr. CaSO_4 , 0.0120 gr. Mg, Na + K together as much as corresponds to 0.0110 gr. Na, and 0.3268 gr. SO_4 ". Thus it is evident that the extract contains about ten times less *magnesium* than *calcium*, and that it contains still less *sodium* together with *potassium*. Thus calcium sulphate predominates absolutely; of course it has to be taken into account that it has in water a limited solubility (about 1.6 gr. in 1 liter of water), which further slightly decreases at a higher temperature.

For the sake of completeness the wet residue after extraction with cold water was submitted immediately to *extraction with* 100 ml. of *hot water* and the solution was evaporated to dryness. The residue after drying at 180°C weighed 0.31 gr. and was then again dissolved and diluted to 250 ml. with distilled water. *Iron* was not present in the solution. According to calculation the whole solid residue (0.31 gr.) was found to be: 0.0556 gr. Ca which corresponds to 0.1889 gr. CaSO_4 , 0.0056 gr. Mg, and 0.1630 gr. SO_4 ". Thus *calcium* again predominates, whereas there is again ten times less *magnesium*. The *alkali metals* were not determined as their main amount must have passed already into the first extract in view of the good solubility of all their compounds.

The residue of the substance after extraction with hot water was further immediately extracted with another 120 ml. of *hot water*, and the extract obtained was investigated separately. After evaporation and drying at 180°C it gave 0.38 gr. of residue, which was investigated in the same way as the preceding ones. In this second extract with hot water were found all in all 0.0698 gr. Ca which corresponds to 0.2369 gr. CaSO_4 , 0.0060 gr. Mg, and 0.1998 gr. SO_4 ". It is evident that here the amount of *magnesium* as compared with that of the *calcium* is still smaller.

To the residue after the second extraction with hot water were added 50 ml. of *hydrochloric acid* (1:1) and after boiling it was diluted with water; the main part was filtered and, after diluting with water up to a volume of 250 ml., it was analysed. In one fifth of the whole filtrate were found 0.0302 gr. Fe, 0.1240 gr. Ca which corresponds to 0.4212 gr. CaSO_4 , and 0.0065 gr. Mg. In this extract there is thus already twenty times less *magnesium* than *calcium*, whereas the *iron* present in the bottom peat scraped off together with the efflorescence is here present indubitably as hydroxide, so that it easily dissolves in the acid solution.

No further extractions were made. As the washing of the insoluble residue would have been very difficult because of the great amount of admixed bottom peat attention was paid in the analyses of all extracts especially only to *the mutual ratio of the compounds determined*. Therefore also the weight of the different residues after evaporation is only of an informative value. From the analyses made it is evident that the extracted sample of the efflorescence contains mainly only calcium sulphate, which, because of its limited solubility and considerable

accumulation, passes constantly into the extracts also when the other components much more easily soluble in water have already long been extracted by water.

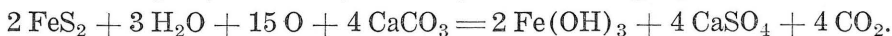
For the sake of completeness and of current orientation also the *water of the two bottom-peat ponds* was examined chemically for certain compounds by a fairly large number of analyses of samples taken in the second half of 1949 and in the first half of 1950. The composition of the two waters did not change much during this time, and I give here briefly only the results of the analyses of the samples taken for examination in November 1949.

In one liter of water from the *smaller bottom-peat pond* situated near the main road were found 0.1032 gr. Ca, 0.0073 gr. Mg. and 0.1012 gr. SO_4 ". For the determination of the *alkalinity* (the *temporary* or *carbonate hardness*) was used for 100 ml. of water 4.1 ml. of 0.1 N hydrochloric acid corresponding to 0.2501 gr. HCO_3' in one liter of water (20.5 degrees of carbonate hardness).

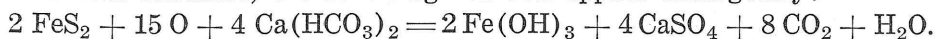
In one liter of water from the *larger bottom-peat pond* situated near the Obora were found 0.0942 gr. Ca, 0.0071 gr. Mg. and 0.0609 gr. SO_4 ". For 100 ml. of water was consumed 4.5 ml. of 0.1 N hydrochloric acid corresponding to 0.2745 gr. HCO_3' in 1 liter of water (22.5 degrees of carbonate hardness).

The waters were not examined for other components. The hydrogen ion concentration of both waters was found $\text{pH} = 7.5$. The waters are not coloured yellow by the peat, but are colourless and clear when they are not stirred up by the ducks and geese. From the analyses made it is evident that the water of both ponds has not only a considerable content of *calcium* and *sulphates*, but also a considerable *alkalinity* as shown by its carbonate hardness. (For comparison I may mention in passing that for 100 ml. of Elbe water taken at the same time below the hydroelectric works only 2.8 ml. of 0.1 N hydrochloric acid were used, thus corresponding to only 0.1708 gr. HCO_3' in 1 liter (14.0 degrees of carbonate hardness). When the water of the small pond had been pumped out prior to the cutting of the bottom peat, a strong current of underground water could be seen at the bottom; this water possesses already indubitably a considerable hardness from the lime marl substratum through which it percolates.

The occurrence of a greater amount of *sulphates* can of course be accounted for only by the alteration of pyrite or marcasite present directly in the lowland moor or perhaps in part also in the deeper layers of the surrounding Cretaceous formation through which the groundwater containing traces of oxygen passes. The alkalinity of the bottom peat binds the sulphuric acid formed by the alteration of pyrite into calcium sulphate, and the simultaneously formed ferrous sulphate turns into ferric hydroxide, which is deposited in the bottom peat as limonite. The whole process of the formation of gypsum and limonite, presupposing that the acidity has been removed by the calcium carbonate present in the bottom peat, can be expressed by the following equation:



Presupposing that the acidity of the products formed by the alteration of pyrite is removed only by percolating groundwater of a considerable carbonate hardness, the following reaction applies analogously:



The carbon dioxide formed is liberated at the surface of the ground and escapes into the atmosphere, or it may after the solution has moved dissolve again the calcium carbonate.

From the above study it is clear that the efflorescences on the lowland moor at Poděbrady are formed by fairly pure crusts of gypsum. As shown by the detailed investigation of the efflorescence and of that portion of the bottom peat which is soluble in water no suitable physico-chemical conditions exist for the formation of *mirabilite*, which had been recorded from the lowland moors near Poděbrady.

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THE PLATE:

Cut bottom peat at the smaller pond. Facing south. To the right in the background the main road leading to Prague.

Foto Dr. Karel Komárek.

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