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Sulfate minerals and their origin in the weathering zone of the pyrite-bearing schists at Wieściszowice (Rudawy Janowickie Mts, Western Sudetes)

ABSTRACT: A model of weathering alterations for the pyrite-bearing schists outcropping at the abandoned pyrite mine at Wieściszowice (Rudawy Janowickie Mts, Western Sudetes, Poland) is proposed as based on the studies of supergene sulfate minerals, as well as shallow groundwaters and surface waters of the region, experimental decomposition of the schists in sulfuric acid solutions, and calculation of the crystal–solution equilibria of rock-forming minerals. Formation of magnesiocopiapite, aluminocopiapite, pickeringite (and its new variety ferropickeringite), fibroferrite, slavikite, gypsum, epsomite, and alunogen is recognized in the studied weathering zone. Analyses of the sulfur and oxygen isotope ratios in sulfate ions, and oxygen and hydrogen isotope ratios in crystallization water, were used to characterize the origin and stability ranges of the studied minerals. Sulfur isotope fractionation among sulfate minerals was interpreted as an effect of crystallization. Oxygen isotope ratios in sulfates indicate water as the main source of oxygen. The best soluble minerals display seasonal changes of isotope composition of crystallization water, which can be likely correlated to composition of atmospheric precipitation.

INTRODUCTION

Zones of the ore mineral weathering are an environment of formation of an abundant and variable group of supergene minerals. Mineralogical and geochemical investigations of the weathering products are a key to understanding the conditions and mechanisms of sulfide mineral oxidation. In addition to the scientific aspects, such studies might have been of practical importance for ore prospection (SMIRNOV 1956). The weathering minerals formed at the outcrops not rarely resulted in the past in discoveries of new ore deposits, and their observations are still an effective and inexpensive prospecting method, especially in the areas geologically poorly recognized. Understanding processes of weathering, mechanisms of mobilization and migration of economically valuable metals is also an important problem for mining and processing of metal ores. Their recognition was a basis of a relatively new method of exploitation of metal ores by the extraction of the oxidized metal compounds from a deposit *in situ*, omitting the expensive mining works. This technology may be of interest during utilization of poor copper deposits, not suitable for classic mining, and it is already applied to copper extraction from old mine dumps (CATHLES 1994). It requires the introduction of an intensive bacterial oxidation of the dispersed ores controlled by aeration and water supplying. In result copper is dissolved, and from the solution it is precipitated by reduction with metallic iron.

The studies of the sulfide weathering become of increasing importance in the environment protection as well. Their results are used for monitoring of the water and soil pollution in the areas of the metal ore-, black- and brown-coal mines, and ore processing plants. Emission of sulfur-bearing gases, especially sulfur dioxide, causes toxic acid rains. Severe problems are also caused by pollution of surface- and groundwaters, and soils in the areas affected by activity of acid products of sulfide weathering. Acid mine waters and seepages from mine dumps, carrying appreciable amounts of sulfates of aluminum, iron and heavy metals may be environmentally dangerous, too (SZCZEPAŃSKA 1987).

Zones of sulfide weathering developed at the outcrops of ore deposits and areas of mining are appropriate testing areas for affection of minerals and rocks by acid sulfur compounds. Studies in such areas may result in determination of durability of minerals in that environment, recognition of dissolution mechanisms and migration paths of the released elements. This permits prognosing the results of degradation in a scale significantly exceeding the present-day global observations.

The present paper describes weathering zone of pyrite-bearing schists at Wieściszowice in Lower Silesia. The zone is unique in Poland due to intensity of the oxidation processes and the amount of the weathering mineral species. The present Author paid a special attention to the paragenesis of the weathering sulfates and their role in formation of the weathering zone. Studies of this group of minerals connected with geochemical and hydrogeochemical characteristics of the environment were used to construct a model of the development of weathering zone of the pyrite deposit at Wieściszowice and to determine the mechanisms of pyrite oxidation.

The region of the abandoned pyrite mine at Wieściszowice has significant scientific value and is a tourist attractive area, thus it should be protected as a natural reserve.

GEOLOGIC SETTING

The pyrite deposit at Wieściszowice occurs in the mountain chain of Rudawy Janowickie in West Sudetes. The chain extends meridionally at a distance of *c*. 18 km from the Bóbr River valley near town of Janowice Wielkie to Kowary Pass and it displays a complex geologic structure. The western part of the chain is formed by granitoid rocks of the Karkonosze massif, and the eastern part by a group of metamorphic rocks, which is a cover of the massif. To the east the metamorphic rocks of Rudawy Janowickie border on the coarse-clastic Culm sediments of the Intrasudetic Trough.

In the lithostratigraphic division in this region, the metamorphic rocks were called the Rudawy Janowickie group, including Leszczyniec volcanic formation (upper) and Czarnów schist formation (lower) of apparently Early Paleozoic age, namely Silurian or Upper Ordovician (TEISSEYRE 1971). Protolith of the metamorphic rocks consisted of pelite and graywacke sediments with carbonate intercalations and of vein, extrusive and locally tuffaceous rocks of the so-called spilite-keratophyre series, metamorphosed in greenschist facies. The rocks bearing glaucophane, albite, epidote and stilpnomelane (WIESER 1978, SMULIKOWSKI 1995), typical of the glaucophane (blueschist) facies, thus indicating high pressure – low temperature metamorphism, are known from this area as well. The Leszczyniec volcanic formation comprises various amphibolites and metavolcanic rocks, greenstones, crystalline schists and gneisses (TEISSEYRE 1973). The Czarnów schist formation includes a variety of crystalline schists, leptinites, quartzites, amphibolites with marble and calc-silicate rock intercalations. The Kowary gneiss group, consisting of several petrographic varieties of gneisses and granite-gneisses, is stronger-metamorphosed and older than the Rudawy Janowickie group, though its age is not defined. The Kowary gneiss group occurs only in the southern part of the Rudawy Janowickie chain. At the border with the Karkonosze granitoid massif some parts of the metamorphic rocks were affected by contact metamorphism, that caused alteration of the schists to hornfelses. The signs of the activity of hydrothermal solutions derived from the Karkonosze massif are abundant in the metamorphic cover. The widely-known polymetal deposits of Miedzianka, Czarnów and Kowary, now exhausted, formed due to this hydrothermal activity.

The Leszczyniec volcanic formation contains a series of the sericite-chlorite schists with pyrite mineralization (Text-fig. 1). This series is traced in a zone *c*. 4 km long, and its thickness does not exceed 100 m. The pyrite-bearing schists crop out in a meridional belt about 200 m broad, from the buildings of the village of Wieściszowice to the eastern slopes of the Wielka Kopa Mt. The schist series is locally intensively folded and dips at the angle of 50-70° to the east. The pyrite-bearing schists form a characteristic level in the upper part of the metamorphic schist profile. JASKÓLSKI (1964) distinguished in the schists sole layers, ore-mineralized level, and roof layers. The sole layers are composed of creamy, compact quartzite schists. In the roof part of the sole layers, directly under the ore-mineralized schists, one may find limonite or cataclasite (schist fragments cemented with limonite) intercalations. In the ore-mineralized zone, the thin-laminated pale-green chlorite-sericite schists are the prevailing rock type. However, deep-green chlorite schists and yellowish, brittle sericite and quartz-sericite schists are to be found. The roof layers consist of thicker-bedded, compact, green chlorite or quartz-chlorite schists. Upwards the schists alter gradually in amphibolite schists and amphibolites, more resistant to weathering, as it is marked by the terrain morphology. The ore-mineralized series contains intercalations of greenstones, being at least in part schistose metavolcanic rocks of basic or acid type. The metavolcanic rocks bear relics of plagioclases and at places relics of potassium feldspars and biotite. Nests and lenses of quartz, arranged according to the rock lamination and quartz veins cutting the lamination are common in the whole schist series. Calcite, rarer dolomite and occasional fluorite are found in the quartz veins.

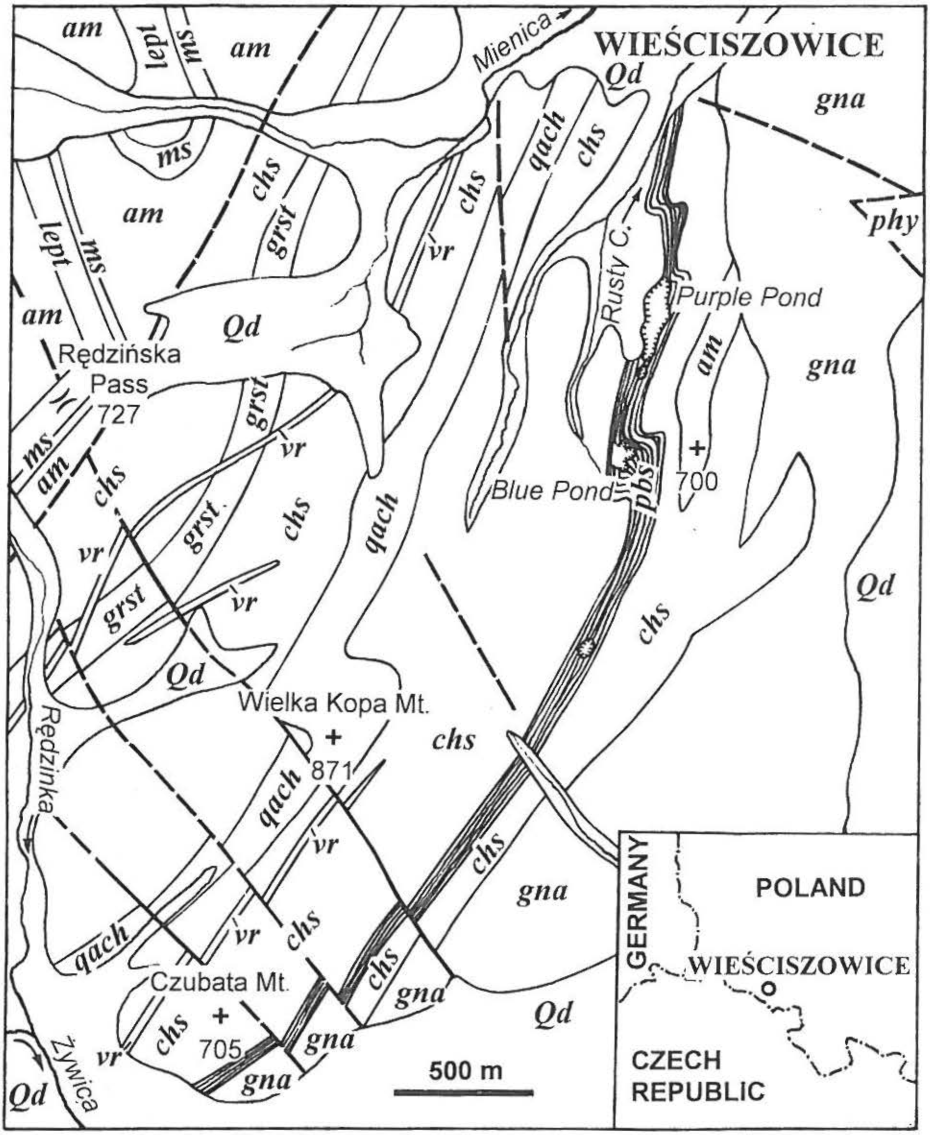


Fig. 1. Geologic sketch-map of the Wieściszowice region in the Rudawy Janowickie Mts, Western Sudetes (*after* TEISSEYRE 1973; *modified)*

Qd – Quaternary deposits, **phy** – phyllites, **gna** – gneisses with amphibolite intercalations, **chs** – chlorite schists, **pbs** – pyrite-bearing schists, **am** – amphibolites, **qach** – quartz-albite-chlorite schists, **grst** – greenstones, **ms** – mica schists, **lept** – leptinites, **vr** – vein rocks

Ore-mineralized sericite-chlorite schists are the most common rock variety in the exploited part of the deposit cropped out in the mine pits. The schists consist mainly of laminae of fine-grained quartz and flakes of sericite and pale-green chlorite occurring in variable proportions. Blasts of albite containing from 2 to 8 % An, and nests or rarer lamellar aggregates of calcite may also be found in the schists. Intercalations of the pyrite-bearing chlorite schists occur in the northern part of the largest mine pit. These rocks, if compared with the previous schist type, have a darker, distinctly green color and less distinct schistosity. They contain less quartz and more intensive green chlorite. Epidote, actinolite, and locally significant amounts of calcite appear in the pyrite-bearing schists.

The increase of the pyrite content is accompanied by a lightening of the schist color, caused by a gradual alteration of chlorite into sericite. Around the pyrite blasts chlorite is usually absent. Pyrite crystals are surrounded by lenticular haloes of palisade quartz grains. In the wedges of the lenses quartz is usually coarser-crystalline than in their centers; clusters of calcite were found in the wedges as well. Layer minerals commonly overflow the pyrite-quartz aggregates. However, locally one may observe schist relics embedded in pyrite blasts, with their edges cutting the quartz halo and schist laminae.

The pyrite mineralization is of impregnation type. Any massive clusters or layer occurrences of pyrite were not found. Euhedral or subhedral pyrite grains have dimensions from tenths to 5 mm, most frequently *c.* 1 mm. The pyrite content in schists ranges from few to *c.* 30 percent. Average pyrite content in the ore series one may evaluate as *c.* 10 percent. The mineral composition of the ores is very uniform. Pyrite is accompanied by only trace amounts of other sulfides. Chalcopyrite is the most common one, forming microscopic inclusions in pyrite in form of emulsion-like exsolution structures or filling cracks in pyrite. Inclusions of bornite, galena and sphalerite are distinctly rarer that these of chalcopyrite. Polymetal mineralization consisting of Cu, Zn and Pb sulfides and antimony sulfosalts of Cu and Pb was found only in quartz veins (PIESTRZYŃSKI & SALAMON 1977). The absence of marcasite, typical of mineralization in metamorphic rocks, is apparent here. Arsenic ores, common in the Variscan mineralization of the Rudawy Janowickie, are unknown in the Wieściszowice ores.

ORIGIN OF THE PYRITE DEPOSIT

Origin of the sulfide deposits, occurring in the metamorphic rocks, is one of the rather difficult problems of the ore geology and in many cases is controversial till present. In the case of the pyrite deposit at Wieściszowice various opinions were published as well. Early in this century the German scientists accepted the primordial sedimentary origin of the deposit, what was supported by mineralization bound to one level of the schists and essentially monomineral composition of the ores (PETRASCHECK 1933). The subsequent metamorphism, according to these opinions, caused only pyrite recrystallization and had no significant influence on the ore accumulation. The mineralization age was determined by the German scientists as younger than Carboniferous, because in the Culm sediments one found pebbles of the pyrite-bearing schists. According to these opinions, the ore mineralization was not related to the tectonic structures, *e.g.* pyrite did not concentrate in zones of the tectonic fissures, microfold crests etc., what should appear if the mineralization would be a product of the solutions generated during regional metamorphic processes. Any indications of the connection of the ore deposit origin with the hydrothermal solutions that stemmed from the granitoid intrusion of Karkonosze are absent as well. The opinion on the lack of such connection is supported by a very simple mineral composition of the ores, quite unlike the composition of the hydrothermal polymetal deposits of the Rudawy Janowickie.

The documentation works, performed by Polish geologists in late 40s and in 50s, and detailed geologic and mineralogical studies submitted new data of genetic importance (KRAJEWSKI 1949, NIELUBOWICZ & JASKÓLSKI 1957). These data indicated rather hydrothermal origin of the pyrite deposit at Wieściszowice. Despite numerous ambiguities, one presented an opinion, that pyrite crystallized from hydrothermal solutions that infiltrated metamorphosed schists. Those solutions caused gradual alteration of the quartz-chlorite schists into quartz-sericite ones and quartzites with pyrite. The solutions could originate during regional metamorphism. However, the possibility of the sedimentary origin of the deposit has not been rejected completely, what meant that one supposed a metamorphic mobilization of the older accumulations of pyrite.

A new and till now most complete hypothesis of the origin of the pyrite deposit at Wieściszowice was presented by JASKÓLSKI (1961, 1964). This author indicated a distinct similarity of the discussed deposit to the pyrite deposits occurring in the greenschist facies rocks of the Urals and Caucasus Mts, whose origin is connected with the submarine extrusions of the spilite-keratophyre lavas. The pyrite deposit at Wieściszowice would be thus of hydrothermal origin (*sensu lato*) connected with subaquatic (oceanic floor) volcanism. More exactly it should be included in the exhalation-sedimentary type of the volcanic deposits. Iron for pyrite crystallization was brought by the basaltic lava extrusions, afterwards submitted to the seawater influence and altered into spilites and keratophyres. Sulfur, according to JASKÓLSKI, could be of magmatic origin or came either from reduction of marine sulfates or from decomposition of organic matter.

HISTORY OF PYRITE MINING

The pyrite deposit at Wieściszowice was discovered in the mid-18th century. Its exploitation started in 1785 in the northern, richest part of the deposit, where the mine "Hope" was located. In 1793 the second mine called "New Luck" started to operate 140 m to the south from the first one, and in 1796 the third mine "Gustav" began exploitation 800 m further to the south (DZIEKOŃSKI 1972). Exploitation was carried by open pit mode with variable intensity, and later in the northern part by the underground workings. The ore after rock crushing was processed by use of a simple gravitation technique on wash tables. One obtained 12-14

Purple Pond, with unusual color of water, filling the bottom part of the abandoned pit mine at Wieściszowice

1

2

1 — Weathered pyrite-bearing schists forming the wall of the mine excavation; exposed part is *c*. 3m high

2 — Multicolored encrustations of sulfate minerals covering walls of the abandoned parts of the pyrite mine wt.% pyrite concentrate containing 47 wt.% of sulfur. The dressed ore was used first for iron and copper sulfate production, and after 1869 for obtaining sulfuric acid. The exploitation ceased in 1925 due to economic reasons. The prospecting and documentation works, carried in 1940s and 50s, did not lead to resumption of the exploitation.

Three separate open pits and two waste dumps improperly located on the non-exploited part of the deposit (Text-fig. 2) are the reminders of the mining works. The dumps occur below the largest, northern open pit of the former "Hope" mine. The pit extending meridionally has length of 430 m, width of 110 m and depth from 30 to *c.* 150 m. The deepest part of the pit is occupied by the so-called Purple Pond. The bottom of the smaller pit "New Luck" hosts the Blue Pond. In the third, smallest pit "Gustav" water is retained only temporarily, forming the Green Pond.

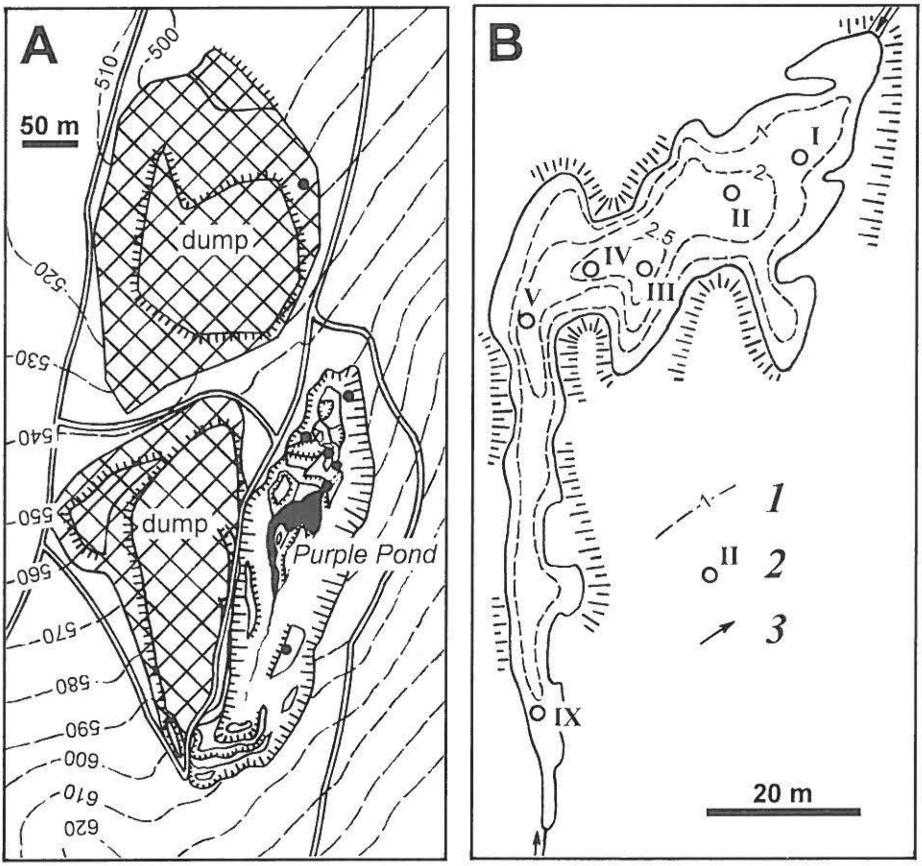


Fig. 2. **A** — Sketch map of the northern pit and dumps of the abandoned pyrite mine at Wieściszowice; dots indicate the occurrence sites of greater accumulations of the sulfate minerals

B — Bathymetric sketch of the Purple Pond

1 – isobaths in meters, **2** – profiles of the water sampling for analyses, **3** – directions of water inflow to the pond

RANGES AND METHODS OF INVESTIGATION

This study aimed to present the model of the development of the pyrite-bearing schist weathering zone, cropped out in the abandoned mine at Wieściszowice. This model bases mainly on the studies of the paragenesis of the weathering sulfate minerals, completed by geochemical characteristics of the weathering rocks and hydrogeochemical investigations of waters outflowing from the weathering zone. The mineralogical and geochemical data concerning pyrite mineralization and barren minerals present in the deposit, obtainable from literature, were applied in the model as well. The analyses of the chemical composition of the main mineral of the schists, that is chlorite, were performed by the Author, because such data were lacking. By the use of the electron microprobe the composition of chlorite in six pyrite-bearing schist samples were performed.

Studies of mobility of the elements released due to weathering of the pyrite-bearing schists are based on the analyses of chemical composition of superficial and shallow-infiltration groundwaters of the debris level. Twenty two components were determined by the AAS and ICP-IAS methods in 46 water samples collected in open pits, seepages from waste dumps, springs and creeks at the mine region (PARAFINIUK 1997). The main physico-chemical parameters of waters (temperature, pH, electric conductivity) were determined directly in the field during sampling. A special attention was paid to the Purple Pond, occupying a part of the northern pit of the mine and collecting soluble weathering products washed out from the surrounding rock walls (Text-fig. 2). A bathymetric sketch of this pond was made and water samples were collected in five profiles for each one-meter-thick layer of water twice a year: in July and in February (from under the ice cover). Mineral composition of the bottom sediments of the Purple Pond and ochre-like precipitates formed in adits and places of water outflows was also analyzed.

Analytical data, referenced in places herein as PARAFINIUK (1997), are presented in an unpublished report, deposited in the Institute of Geochemistry, Mineralogy and Petrography, University of Warsaw.

On the basis of the performed analyses one determined the saturation of waters with respect to the mineral phases occurring in the environment or potentially present ones by means of the computer program WATEQ4F (PLUMMER & *al.* 1976). This procedure made possible the determination of stability ranges of the minerals under the weathering conditions and recognition of the source minerals of the elements released in the weathering zone.

Computer calculations were afterwards verified in part by experimental decomposition of the pyrite-bearing schist in sulfuric acid solutions of various concentrations. Ground one-gram schist samples without signs of weathering were shaken for 14 days with 100 ml of 0.01-, 0.1-, 1-, 2- and

5-molar H_2SO_4 solutions, and with distilled water as blank sample. Filtered solution was analyzed by chemical methods and the undissolved remainder was examined to determine its phase composition by X-ray diffraction.

During several-year-observations of the weathering zone one collected several hundreds of sulfate mineral specimens, about one hundred fifty of them were selected for detailed studies. Representative specimens of some sulfate minerals were donated to several mineralogical museums (Museum of the Earth in Warsaw, University Museum in Göttingen) for comparative studies. Identification of minerals formed in the weathering zone was mainly performed by means of the X-ray powder diffraction patterns, though for exact identification of the minerals with many isomorphic replacements it was necessary to make chemical analyses. Moreover, the results of differential thermal analysis were used. Samples of the minerals, especially these of the sulfate group, were collected in various seasons of the year to recognize seasonal changes of composition of the paragenesis and to determine the zoning of the mineral occurrence and stability ranges. The samples were saved from humidity changes to prevent their possible decomposition.

Complete characteristics are presented for four selected minerals: slavikite, fibroferrite, copiapite, and pickeringite. The studies included determination of occurrence forms of these minerals by means of the SEM method, X-ray powder diffraction patterns (with the unit cell parameters determination for slavikite and pickeringite), chemical ICP-IAS determinations of main and trace elements and DTA analyses. Results of the spectroscopic studies of these minerals are not included in the present paper and they will be published elsewhere. Other minerals of the paragenesis either occur in amounts too small for their separation or they are common and formerly investigated enough to omit their renewed studies. All the minerals of the paragenesis were taken into account during the considerations on the origin and evolution of the studied weathering zone.

A special attention was paid to the analysis of the isotope ratios in the sulfate minerals. Isotope composition of sulfur and oxygen of sulfate ion and oxygen and hydrogen of crystallization water in the sulfate minerals were determined. Such complex and extended range of the isotope studies was performed for the first time for weathering minerals, according to the present Author's knowledge. These studies were carried to verify the importance of the isotope methods in the investigation of the sulfide weathering and to attempt a reconstruction of the mode of the weathering process. Isotope composition of sulfur and oxygen was determined in over thirty samples of gypsum, fibroferrite, copiapite, pickeringite, epsomite, and sulfates dissolved in water of the Purple Pond. Moreover, sulfur isotope composition was determined in six pyrite samples. Sulfate minerals for sulfur isotope determinations were dissolved in distilled water with

HCl added, sulfates were precipitated from the solute as $BaSO_4$. The latter after washing was reduced to SO_2 by use of the method described by HAŁAS & WOŁĄCEWICZ (1981). Pyrite was oxidized by concentrated HCl and HNO_3 with Br_2 added to obtain sulfate ion, next precipitated as $BaSO_4$. Further procedure was the same as for sulfate minerals. Isotope analyses of oxygen in sulfates were performed in CO_2 produced from $BaSO_4$ by reduction with graphite (MIZUTANI 1971).

Gypsum, copiapite, pickeringite, and fibroferrite were selected for studies of the isotope composition of crystallization water. Samples of these minerals and samples of water from Potok Rdzawy (Rusty Creek) were collected in one-month intervals during the whole year 1991. Mineral samples were heated under vacuum conditions till their complete dehydration. Hydrogen for isotope analyses was obtained from the separated water by reduction with metallic zinc (COLEMAN & *al.* 1983). Isotope composition of oxygen in water was determined by calibration method of EPSTEIN & MAYEDA (1953) in the system CO_2 — H_2O. The isotope ratios of the investigated elements were determined by two-collector method with a modified mass spectrometer MI-1305. The determination results are given as the values of $\delta^{34}S$ relative to the troilite standard CDT, and $\delta^{18}O$ and δD relative to the SMOW standard. Isotope determination errors do not exceed 0.2‰ for sulfur and oxygen analyses, and 2‰ for hydrogen analyses.

HYDROGEOCHEMICAL FEATURES OF THE STUDIED AREA

Weathering of the pyrite-bearing schists is the reason of formation of a local hydrogeochemical anomaly in the environs of the abandoned mine. This anomaly is dramatically visible both in superficial and in shallow debris level groundwaters (MICHNIEWICZ 1978, BALCERZAK & *al.* 1992). The anomaly is characterized best by water composition of Purple Pond in northern open pit. This small reservoir *c.* 100 m long, less than 20 m wide and *c.* 3 m deep (*see* Text-fig. 2) attracts the attention by unusual red-brown color of its water and is of local tourist interest (Pl. 1). It is supplied with water by several seepages from the exploitation pit, but it has no any superficial outflow. Apparently there exists a hidden outflow through crack network and underground workings of the mine. In spite of the seasonal changes of the water level, the reservoir did not dry out even in extremely arid years. Chemical composition of water in the Purple Pond is influenced by weathering processes of the pyrite-bearing schists and it may be treated as an indication of the course and intensity of these processes. The pond water collects the soluble weathering products, removed by precipitation water from the pit walls. However, the soluble salt concentration do not reach the crystallization point, seemingly due to an outflow of the more salt-rich bottom water by infiltration through fractures in rock massif. The investigations of the bottom sediments did not reveal gypsum or other soluble minerals. These scarce in amount sediments consist of detrital minerals supplied by schists and small admixture of iron hydroxides.

In the laboratory crystallization run, at room temperature, gypsum started to crystallize from water of the Purple Pond after evaporation of a half of the volume of this natural solution. Lausenite $Fe_2(SO_4)_3 \cdot 6H_2O$ and magnesium sulfate crystallized from the last portion of the solution; after certain time these compounds altered to copiapite.

Chemical composition of water from the Purple Pond has features typical of an area of the sulfide oxidation. Water is strongly acidified with sulfuric acid, what results in pH of 2.6–2.8. Total dissolved salts (TDS) ranges from 3 to 5.5 g per liter (Table 1). The water belongs to the sulfate-calcium-magnesium type, according to the SHCHUKAREV-PRIKLONSKIY'S classification. Calcium content varies from 200 to 300 mg per liter and that of magnesium from 150 to 250 mg per liter. Appreciable concentrations (all in mg per liter) were found for iron: 380–600, and for aluminum: 90–170, whereas alkali metals are low, as indicated by very stable value of sodium in all profiles: *c.* 5, and variable one for potassium: 0.1–0.9. The alkali concentrations are lower than general background value for groundwaters of the temperate climatic zone and they confirm the scarcity of potassium in schist minerals, typical of all the rocks of the Leszczyniec volcanic formation (*see* SMULIKOWSKI 1995). Concentrations of heavy metals are distinctly elevated, as it is common in weathering zones of the sulfide deposits. One found in water from the Purple Pond (in mg per liter) manganese 35, copper 36, zinc 0.5–1.6, nickel 0.3–0.6, cobalt 0.4–0.7, chromium 0.2, and traces of cadmium, vanadium and lead. Sulfate is the prevailing anion (2,500–4,300 mg per liter); chlorides occur in concentrations from 3 to 15 mg per liter, thus their average is lower than the mean value for groundwaters of the temperate climate. Due to low pH, bicarbonate ion is practically absent in the water of the discussed area. One found fluoride (0.5–2.5 mg per liter) and phosphate (up to 2.6 mg per liter) anions. The high silica content (70–87 mg per liter) occurs typically in waters of acid zones of the sulfide weathering.

Contents of the main components in the water samples of the studied profiles increase gradually downward both in the summer and in the winter season. Contents of the minor and trace elements are more uniform. Any significant difference of the water composition for samples, collected during the summer or winter seasons, was not observed.

In the specific hydrochemical environment of the Purple Pond there exists an unusual assemblage of acid-tolerant organisms, not investigated sufficiently in ecological aspects till present. Preliminary observa-

Table 1

Chemical composition of selected water samples from Wieściszowice region (in mg/l)

Sample	II/1		II/2		II/3		V/1	
	A	B	A	B	A	B	A	B
T,^{0}C	18	4	18	4.5	18	4.5	18	4.5
pH	2.59	2.67	2.58	2.57	2.55	2.57	2.60	2.58
$\varkappa$ mS/cm	4.02	3.69	4.12	4.03	4.60	4.39	3.97	4.03
Fe_{tot}	389	432	420	526	462	541	378	443
Ca	212	258	210	257	206	283	200	239
Mg	177	150	188	156	209	203	180	143
Al	90.6	101	91.5	113	105	141	88.2	101
Na	4.9	5.5	4.9	5.0	5.1	5.1	4.9	4.9
K	.13	.3	.12	.5	.18	.1	.11	.2
Sr	.26	.26	.26	.25	.28	.28	.24	.24
Mn	3.08	3.34	3.39	3.67	3.92	4.23	3.03	3.29
Cu	3.16	2.74	3.34	2.86	3.56	3.69	3.16	2.60
Zn	.60	.65	1.13	.78	1.65	.87	.59	1.14
Ni	.35	.39	.38	.51	.42	.56	.34	.41
Co	.49	.45	.51	.50	.57	.58	.48	.45
Cr	.20	.17	.21	.21	.21	.23	.16	.18
Cd	nd.	.02	nd.	.01	nd.	.02	nd.	.02
V	.1	.07	.1	.08	nd.	.08	nd.	.07
SiO_2	77.5	80	80.2	83	82.6	85	73.2	77
SO_4	2734	2932	2913	3329	3467	3744	2761	2906
Cl	8.6	3.8	14.8	3.1	12.5	3.5	6.4	4.0
F	.73	.79	.63	.86	.91	1.92	1.35	.56
PO_4	.60	.96	.50	2.48	.40	1.96	.35	1.00

nd. — not detected

II/1, II/2, II/3 – Purple Pond water profile; depth 0, 1.0 and 2.1m, respectively;

V/1, V/2 – Purple Pond water profile; depth 0, 1.0m, respectively;

VII – small seepage from dumps; X – large seepage from dumps;

XI – springs below the mine;

A – Sampling in July 1991; B – Sampling in February 1992; C – Sampling in October 1992

tions indicate that this assemblage of organisms living in such severe, unfavorable conditions is surprisingly abundant. It includes numerous microorganisms, especially sulfur bacteria *Thiobacillus ferrooxidans,* radiolaria and euglenas; the shallow parts of the reservoir are inhabited by colonies of filamentous algae. One may observe even small aquatic invertebrates.

Chemical composition of water forming seepages at the foot of dumps is similar to that of the Purple Pond (Table 1). The solute composition is formed due to a long-time contact of the fine-grained loose rock material still bearing appreciable amount of pyrite with infiltrating precipitation water. The composition is representatively shown by the sample taken from a small seepage marked with number VII. The total dissolved salts are high, sometimes exceeding 6 g per liter. Contents (in mg per liter) of iron (1,000), calcium (400), magnesium (350) and sulfate (4,500) are

Table 1 *(cnt'd)*

V/2		VII			X		XI
A	B	A	B	C	A	B	A
15	4.5	11	6.5	4.2	8	6	8
2.60	2.55	2.89	2.79	2.72	2.72	2.69	8.75
4.03	4.27	4.56	4.59	4.16	3.68	3.72	.22
382	500	668	579	1023	218	236	<.05
99.9	271	160	379	403	173	309	53.0
180	190	345	248	329	177	173	12.6
92.5	133	50.9	77	49	65.7	94	<.05
5.1	5.0	5.1	4.4	5.6	5.6	5.9	4.2
.13	.7	2.6	2.4	2.3	.6	.6	.3
.24	.27	.77	.51	.68	.39	.35	.05
3.14	4.03	10.3	8.18	14.2	3.48	3.59	<.01
3.17	3.28	2.30	2.57	1.44	2.02	2.45	<.01
1.23	.90	1.12	1.03	1.11	.49	.55	<.01
.35	.51	.37	.32	.50	.24	.27	<.01
.48	.55	.76	.61	.99	.40	.39	<.01
.18	.23	.02	.03	.01	.09	.10	<.01
nd.	.02	nd.	.02	.03	nd.	.01	<.01
nd.	.08	nd.	nd.	nd.	nd.	nd.	<.01
73.2	82	62.6	64	45	73.3	69	8.5
2862	3499	3759	3527	4520	2389	2603	47.0
7.3	3.4	4.8	2.3		7.6	6.3	12.4
1.09	1.32	1.35	1.05	1.5	1.55	1.18	.2
.35	.90	.35	1.1	tr.	.2	.1	.01

high, concentrations of other main components do not differ significantly from those of the Purple Pond. Even lower concentration of chloride and two- to three times higher amounts of manganese and potassium are worth noting here. The calculations indicate, that water outflowing from the dump reach in certain cases saturation state with respect to calcium sulfide and gypsum may crystallize from this solution. Relatively large seepage named No. X of uniform flow and temperature during the whole year has solute composition analogous to that of the Purple Pond. Apparently that it is an outflow from the Purple Pond through debris level and underground workings of the mine. Chemical compositions of water outflowing from the adit, and supplying the Purple Pond, and that flowing from the pit wall to the debris-filled shaft of the mine are similar to composition of water of the Purple Pond. However, they have the total dissolved salt content two times lower though the proportions of the components are the same.

Samples of water collected from springs above and below the mine area (sample No. XI), and surface waters of the Blue Pond and Rusty Creek above the northern pit of the mine (*see* BALCERZAK & *al.* 1992) have a different composition. Their total dissolved salts are much lower (120 to 230 mg per liter); they have higher pH, and heavy metal contents does not exceed the hydrogeochemical background values of groundwaters. Beside sulfate amounting from 50 to 130 mg per liter, they contain chloride from 4 to 12 mg per liter and bicarbonate from 9 to 65 mg per liter. Their waters drain the debris level of schists, gneisses and amphibolites of the overlying rock series, and their contact with the environment of the weathering pyrite-bearing schists is very limited. Due to intensive exchange they do not achieve the composition typical of the sulfide weathering zone.

GEOCHEMICAL PROPERTIES OF THE WEATHERING ZONE

Geochemical processes forming the weathering zones of sulfides, including the type and kinetics of chemical alterations, may be determined on the basis of the chemical composition of the aqueous solutions generated by these processes. Such approach was applied many times, *e.g.* to determine the rate of rock weathering under influence of the acidified environment (PAČES 1985), or in the studies of the pyrite-bearing waste dumps of coal mines (SULLIVAN & *al.* 1986, SZCZEPAŃSKA 1987). To determine which mineral phase is unstable in the oxidation zone and will be dis-

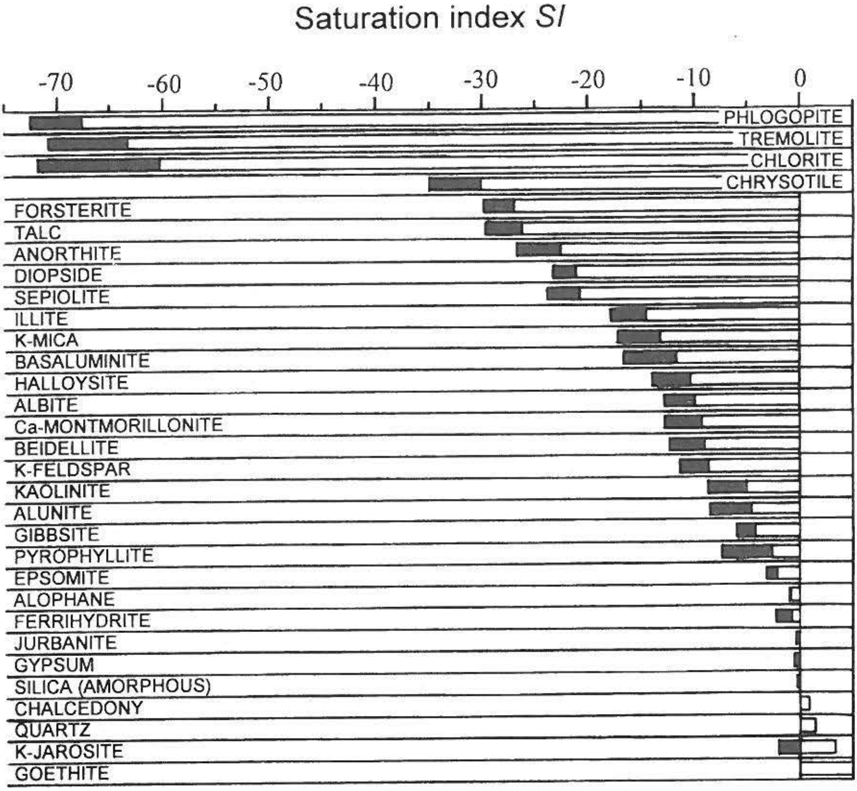


Fig. 3. Minimum and maximum values of the saturation index (*SI*), calculated from chemical composition of waters in the Wieściszowice mine region

solved, and which mineral is stable or may be formed, one may use its saturation index (SI) defined by the equation:

$$SI = \log IAP - \log K_{sp} \tag{1}$$

where IAP – ionic activity potential of the solution components, K_{sp} – solubility constant of a mineral phase at a given temperature. At the equilibrium state SI equals zero; the higher absolute value of SI the more distant equilibrium state and the negative values mean undersaturation of the solution and a possibility of dissolution of a given phase.

Results of the calculations performed by the use of the WATEQ4F program (BALL & *al.* 1987) indicate (Text-fig. 3), that chlorite is the least stable silicate mineral of the weathering schists (SI values lower than -60). Feldspars have SI values c. -10, thus are less unstable, though not in equilibrium with solution; similar unstableness is displayed by micas and clay minerals (smectites and kaolinite). Quartz, hematite and goethite are stable in the studied environment. The solution is saturated with respect to certain weathering minerals, namely to hydronium-, potassium- and sodium jarosite, but not with respect to alunite. Some water samples are either saturated or close to saturation with respect to gypsum.

Recently, kinetics of decomposition of silicate minerals in acid environment is a task of numerous experimental works, carried to recognize the influence of acid rains on the environment (SVERDRUP 1990). On that basis one accepts that the dissolution (decomposition) rate of a mineral depends on the durability of the surface activated complex, formed at the first stage of the process. In the case of chlorite the stoichiometric decomposition may be expressed (SVERDRUP 1990) by the equations:

$$Mg_3Fe_3AlSi_3O_{10}(OH)_7 + 11.2H^+ \rightarrow 3Mg^{2+} + 2.6Fe^{2+} + H_{11.2}Fe_{0.4}AlSi_3O_{10}(OH)_7 \tag{2}$$

and the formed surface activated complex decomposes afterwards:

$$H_{11.2}Fe_{0.4}AlSi_3O_{10}(OH)_7 + 2.8H^+ \rightarrow Al^{3+} + 0.4Fe^{2+} + 7H_2O\cdot H_7Si_3O_{10}^- \tag{3}$$

These equations indicate that at the initial stage of chlorite decomposition, magnesium and a part of iron from octahedral layer are released first to solution. Further degradation of chlorite leads to complete release of iron and mobilization of aluminum from tetrahedral layers.

Computer calculations confirm the experimental studies of decomposition of the pyrite-bearing schist in sulfuric acid solution (Text-fig. 4 and Table 2). Chlorite is an unstable, easily-decomposing mineral of the schists. Its content in undissolved part decreases systematically if the acid

Table 2

Chemical composition of water extracts produced by decomposition of 1g pyrite-bearing schist in 100 cm² H_2SO_4 solutions within 14 days; concentrations dissolved compounds in mg/1g schist

Component	H_2SO_4				
	0.01 M	0.1 M	1 M	2 M	5 M
MgO	4.78	10.58	20.17	25.54	31.41
FeO total	2.70	5.61	10.03	12.34	14.87
Al_2O_3	6.15	11.82	20.54	25.30	30.32
SiO_2	11.56	29.75	46.01	31.89	2.78
MnO	.03	.07	.13	.17	.21
K_2O	.20	.24	.28	.25	.24
Na_2O	.23	.34	.17	.11	.00

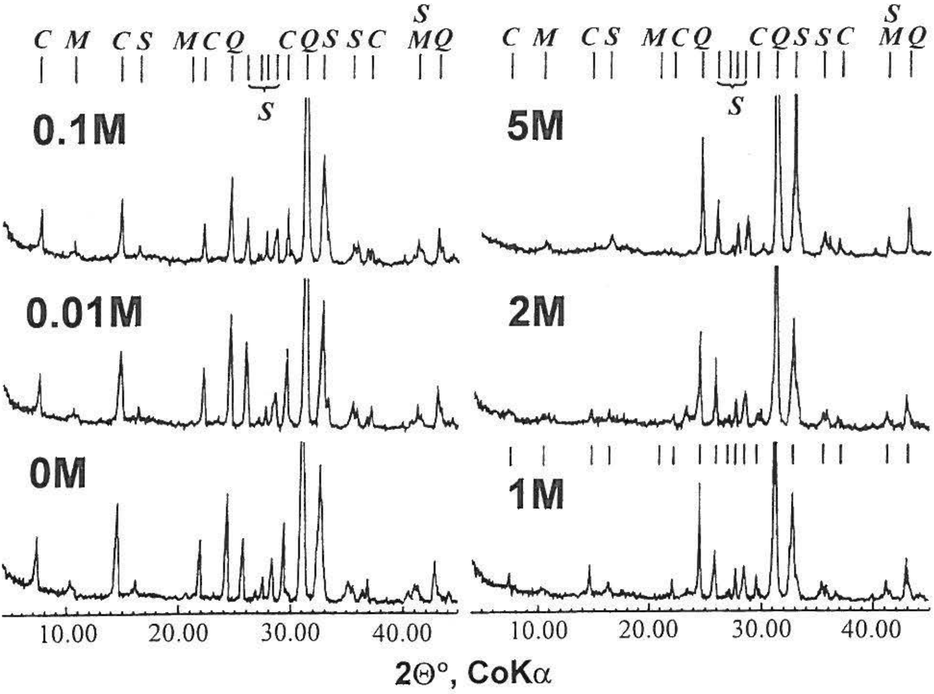


Fig. 4. X-ray powder patterns of samples of the pyrite-bearing schist, treated with aqueous solutions of sulfuric acid (concentrations 0.01M to 5M)

C – chlorite, **M** – sericite, **Q** – quartz, **S** – albite concentration increases. In the 5-molar solution chlorite dissolved completely. It is the only mineral, whose dissolution was observed in the experiments performed by the present Author. Contents of quartz, feldspar (albite) and muscovite during the experiment did not change. Chemical analyses of the post-run solutions indicated, that appreciable amounts of MgO (5 to 31 mg), Al_2O_3 (6 to 30 mg) and FeO (3 to 15 mg) dissolved from decomposing chlorite. Silica content in solution increased from 11 mg in 0.01 M sulfuric acid to 46 mg in 1 M sulfuric acid, and subsequently decreased to 3 mg in 5 M sulfuric acid, probably due to precipitation in the very acid environment. The analyses confirmed low alkali contents in the solution (0.1 – 0.3 mg) independently of the concentration of the sulfuric acid used. Both Na_2O and K_2O could come from a source different than the decomposing schist. Of the heavy metals only manganese is a solute coming from the schist in appreciable amount (from 0.03 to 0.2 mg), what suggests that in the waters it stemmed mainly from decomposed chlorite. The contents of Cu, Zn, Co, Ni, Cr, V, Cd, and Pb in the solutions do not exceed in any case 0.01 mg per 1 g schist leached. This probably results from a poor solubility of pyrite in sulfuric acid, whereas the listed heavy metals are essentially connected with pyrite as mineral inclusions and isomorphic admixtures. Moreover, calcium occurred in the solution in the amounts of less than 0.01 mg, because the treated schist did not contain calcite, easily soluble in acid environment.

In the above-presented context, the chemical composition of the chlorite occurring at Wieściszowice is discriminative for the geochemical features of the studied weathering zone. In thin sections one may distinguish two varieties of this mineral: the rock-forming fine-flaky chlorite of grass-green color, and pale-colored to almost colorless one appearing around pyrite blasts. JASKÓLSKI (1964) identified the first variety on the basis of its optical properties as diabantine and the second one as pennine. Till present their chemical compositions were not determined, thus the given electron microprobe analyses are the first ones ever performed (Table 3). The obtained results show a good chlorite stoichiometry, except for the analyses 2 and 4. According to the suggestion of JIANG & *al.* (1994), who evidenced, that usually alkalis and calcium in chlorite microprobe analyses come from foreign phase contamination, one may consider in this case as well an influence of an acid plagioclase. The structural formula, calculated on the basis of a mean of the four analyses, is as follows:

$$Fe_{2.23}Mg_{2.14}Mn_{0.06}Al_{1.47}[Si_{2.74}Al_{1.26}O_{10}(OH)_8].$$

According to the classification proposed by WIEWIÓRA & WEISS (1990), the chemical composition of the studied chlorites locate them almost in the mid-

Table 3

Chemical composition of chlorite from pyrite-bearing schists

Component	1	2	3	4	5	6
MgO	13.11	11.56	13.09	12.03	12.75	12.32
Al_2O_3	20.34	20.55	21.07	21.41	20.82	20.81
FeO tot.	23.36	24.67	24.21	22.83	24.04	23.82
MnO	.50	.61	.66	.48	.71	.61
Na_2O	.17	.46	.20	1.21	.18	.32
K_2O	.02	.05	.00	.01	.00	.04
CaO	.00	.18	.06	.04	.00	.02
TiO_2	.00	.00	.03	.00	.08	.00
Cr_2O_3	.03	.04	.00	.00	.00	.02
SiO_2	25.61	26.05	24.19	28.97	24.19	24.12
total	83.14	84.17	83.51	86.98	82.77	82.08
Mg	2.16	1.90	2.17	1.89	2.13	2.08
Fe^{2+}	2.16	2.28	2.25	2.01	2.25	2.25
Mn	.05	.06	.06	.04	.07	.06
Al(VI)	1.48	1.55	1.50	1.69	1.46	1.50
Al(IV)	1.17	1.12	1.31	.96	1.29	1.27
Si	2.83	2.87	2.69	3.04	2.71	2.73
Σcat.	9.85	9.79	9.93	9.63	9.91	9.89
$d(001)_c$	14.16	14.16	14.15	14.17	14.15	14.15

dle of the field determined by the clinochlore-chamosite-ripidolite-sheridanite end members (Text-fig. 5). The chlorite composition is uniform, thus it does not confirm the presence of two chlorite varieties, possibly due to a limited number of analyses. Compared with the optic determinations by JASKÓLSKI (1964), the chlorite is a variety richer in aluminum, however, with the composition typical of metamorphic schists. The measured value of the basal X-ray reflection d(001) equal 14.15 Å, as well as that one, calculated on the basis of the chemical composition, indicate the presence of the true trioctahedral chlorite.

The differences in element proportions of the main chlorite components, determined by the electron microprobe analyses (Table 3), and, on the other hand, dissolved in sulfuric acid (Table 2), are difficult to explanation. In the process of the acid decomposition, if compared with magnesium and aluminum, less iron passes to the solute than it is present in chlorite according to the microprobe analyses. Except possible analytical errors, the observed difference may appear due to variations of the chemical composition of that mineral. The microprobe analyses were performed on fresh chlorite crystals, whereas the bulk dissolved chlorite contained also the altered grains surrounding pyrite blasts.

The experimental runs, carried during a relatively short time interval, cannot explain all the geochemical aspects of the weathering. Decomposition of some silicates may develop sufficiently slowly to be omitted in the experiment results, despite an applied concentration of sulfuric acid, much higher than in natural conditions. This supposition most probably concerns micas and feldspars. The increase of potassium concentration in waters, outflowing from the dumps, where contact of the acidified solutions with the disintegrated rock is much longer than in the experiment performed, suggests an ongoing decomposition of micas and/or feldspars, however, at a much lower rate than chlorite degradation.

Mechanism of pyrite oxidation, the most important process in the weathering zone, causing acidification of the environment and a release of iron and the associated heavy metals, is discussed in the further part of the paper. Exact data on the trace element contents in pyrite from Wieściszowice lack, but analyses of pyrite from genetically similar, impregnation pyrite of the Kaczawa Mts yielded average 395 ppm Cu, 430 ppm Pb, 84 ppm Co, 38 ppm Ni, 70 ppm V and 72 ppm Mn (KOWALSKI 1977). Values of a similar order may be expected for these elements in pyrite from Wieściszowice as well.

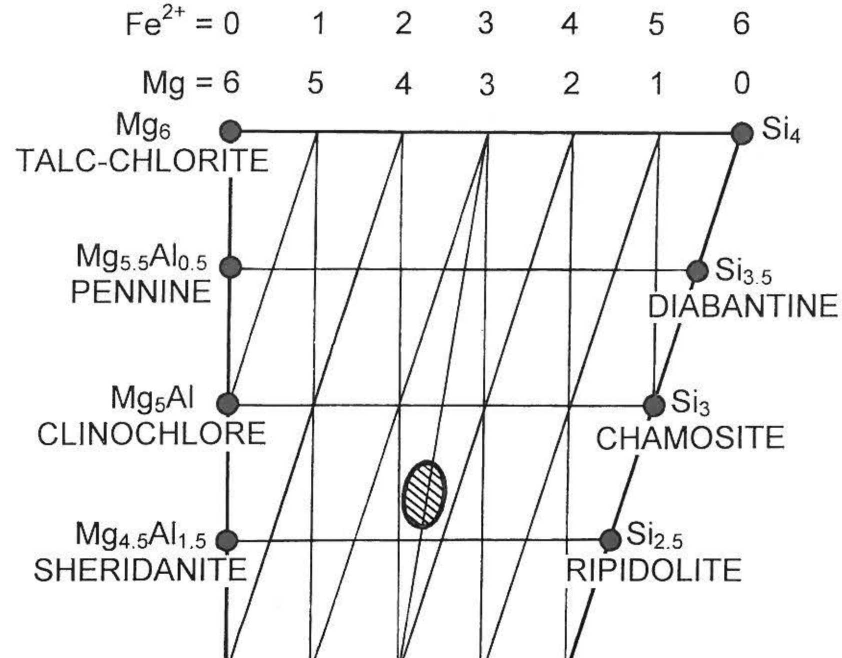


Fig. 5. Composition of chlorite from the pyrite-bearing schists at Wieściszowice (*hatched area*) in the projection field of the trioctahedral chlorites Mg-Fe^{2+}-Al (*after* WIEWIÓRA & WEISS 1990)

Chemical composition of waters of the weathering zone and weathering minerals formed there is essentially influenced by pyrite oxidation yielding Fe, Cu, Ni and other heavy metals and sulfate ions, decomposition of chlorite submitting Mg, Al, Fe, Mn and SiO_2, and dissolution of calcite introducing Ca in the waters. Degradation of other minerals is not excluded, but it does not display any essential role because of their low decomposition rate or rare occurrence. It is worth noting, that iron is mobilized during weathering of the Wieściszowice deposit not only from pyrite but also from chlorite.

SULFATE MINERALS OF THE WEATHERING ZONE

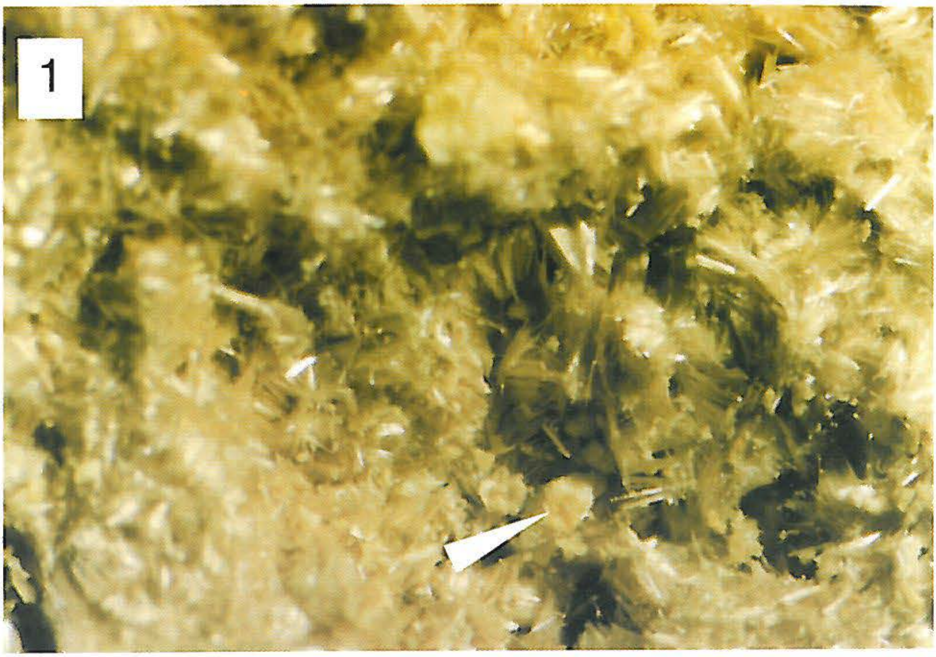
Development of the ore weathering zones and their mineral composition typically are very variable. This is caused by mineral composition of the ores, kind and chemical composition of the wall rocks, and climatic conditions (total precipitation and its annual changes, temperature, water table level). These factors cause that even the same ore parageneses in the oxidation process may result in different weathering zones of quite variable mineral compositions.

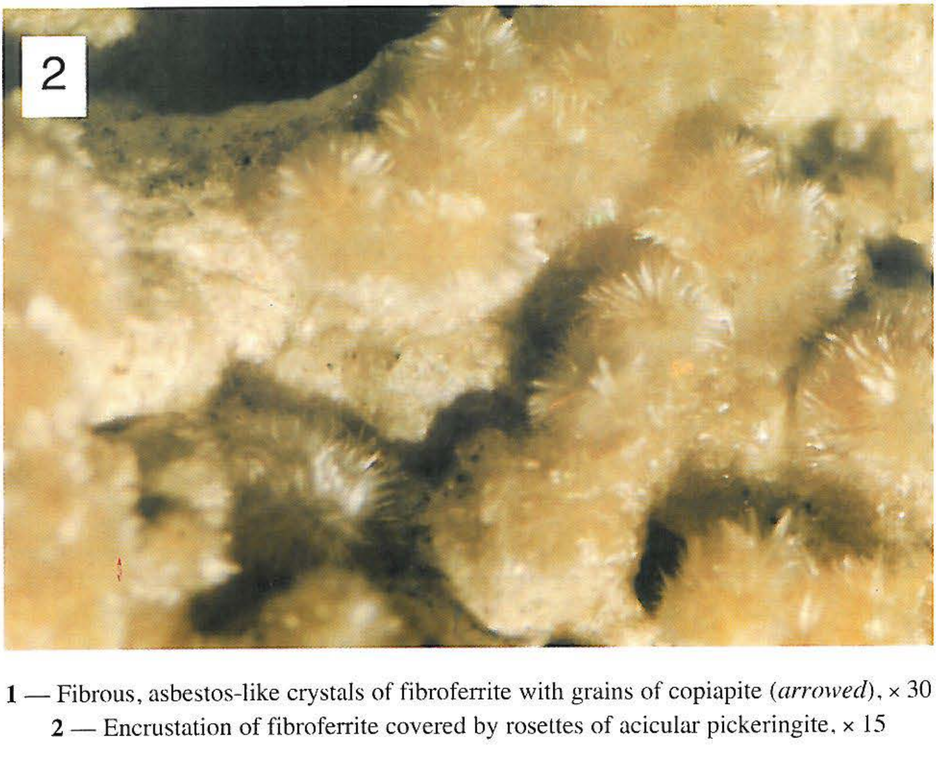
Weathering zone of the pyrite-bearing schists at the Wieściszowice mine is a crystallization environment of rich sulfate parageneses (Pls 2-14). Despite a common knowledge of this outcrop, these parageneses were not studied in details. However, a number poorly-founded circulating opinions was bound to this location, afterwards not confirmed by thorough studies. Till present the best data were published by KUBISZ (1964), who identified copiapite and halotrichite at Wieściszowice and included valuable X-ray, chemical and thermogravimetric results, evidencing presence of magnesiocopiapite. The occurrence of jarosite, suggested by WRZODAK (1962), was not confirmed, whereas the presence of gypsum did not cause any doubt (JANECZEK & *al.* 1991).

Several-year observations of the present Author allowed to extend significantly the list of the weathering sulfate minerals from Wieściszowice. Copiapite, pickeringite, fibroferrite, slavikite, melanterite, gypsum, epsomite and alunogen (Text-fig. 6) were found in the sampled material; probably this is not a final list and one may even expect new findings. Pickeringite, fibroferrite and slavikite were till now unknown from the area of Poland.

Slavikite

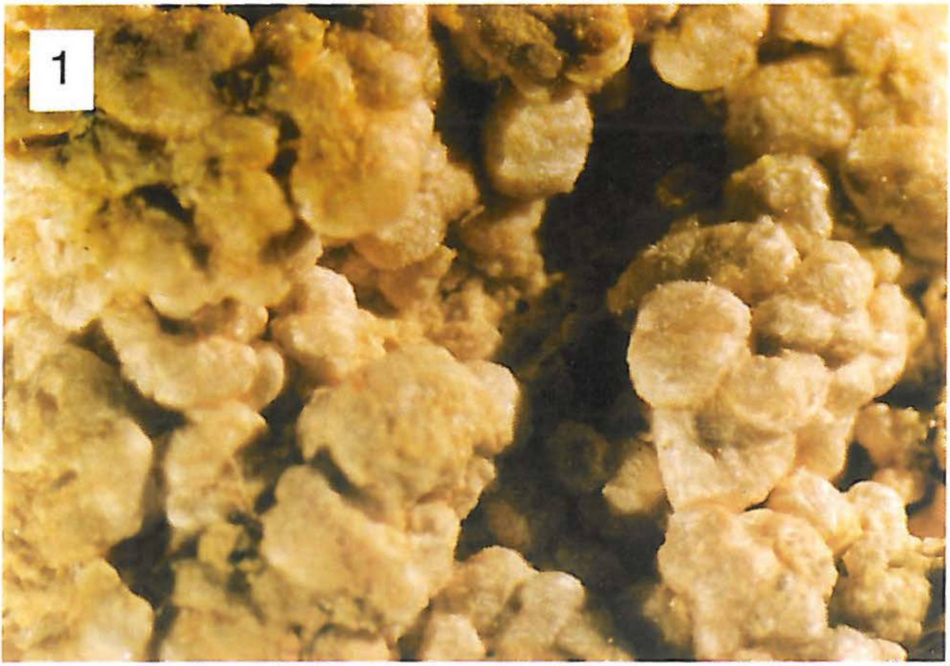
This mineral belongs to the group of hydrous basic sulfates and is still a poorly studied species with controversial even main features and proper-

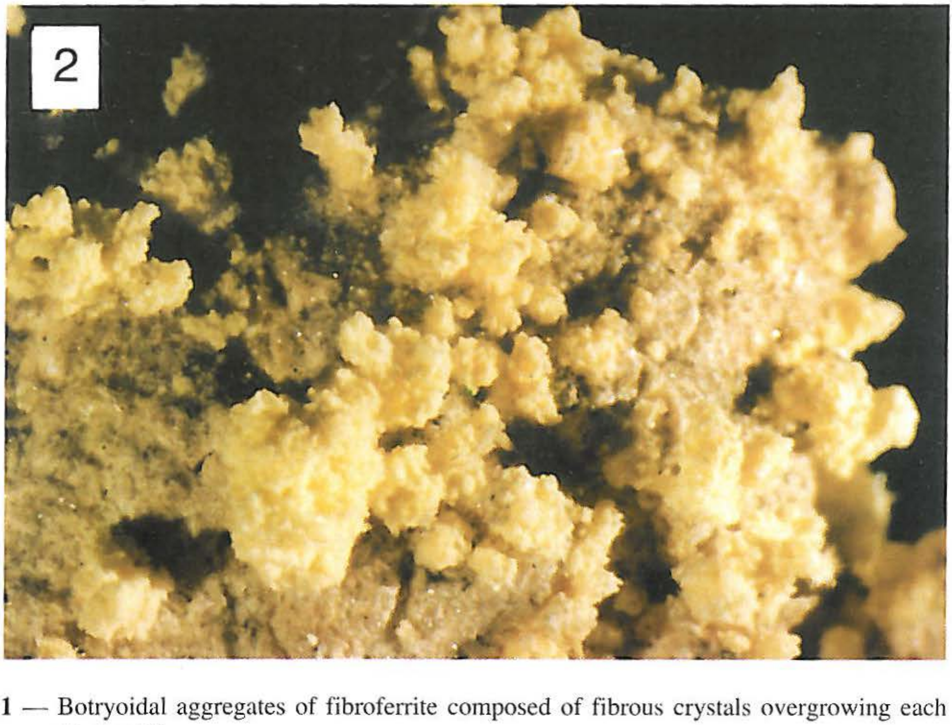




1 — Fibrous, asbestos-like crystals of fibroferrite with grains of copiapite (*arrowed*), × 30

2 — Encrustation of fibroferrite covered by rosettes of acicular pickeringite, × 15



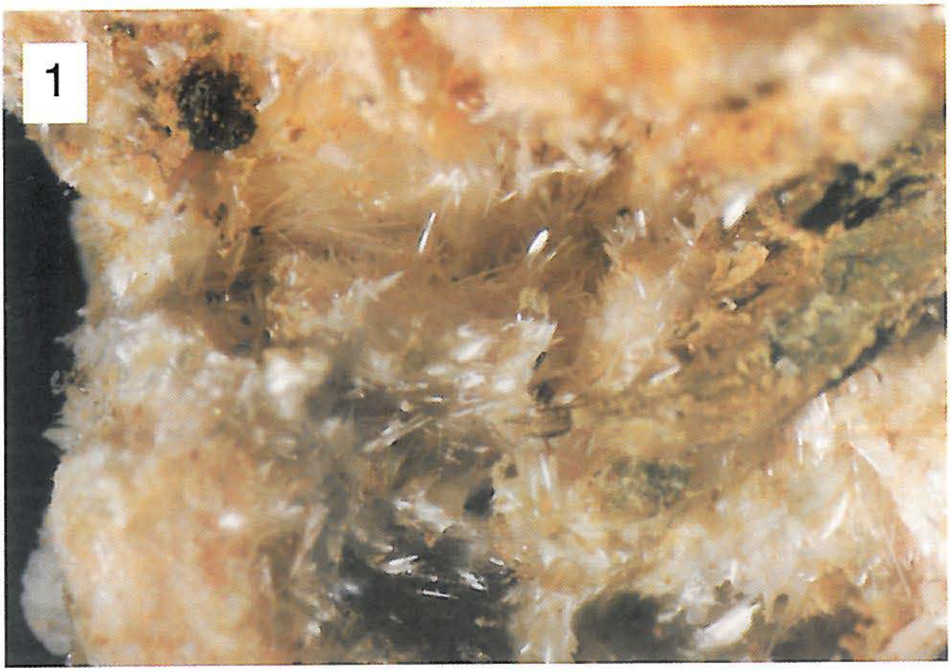


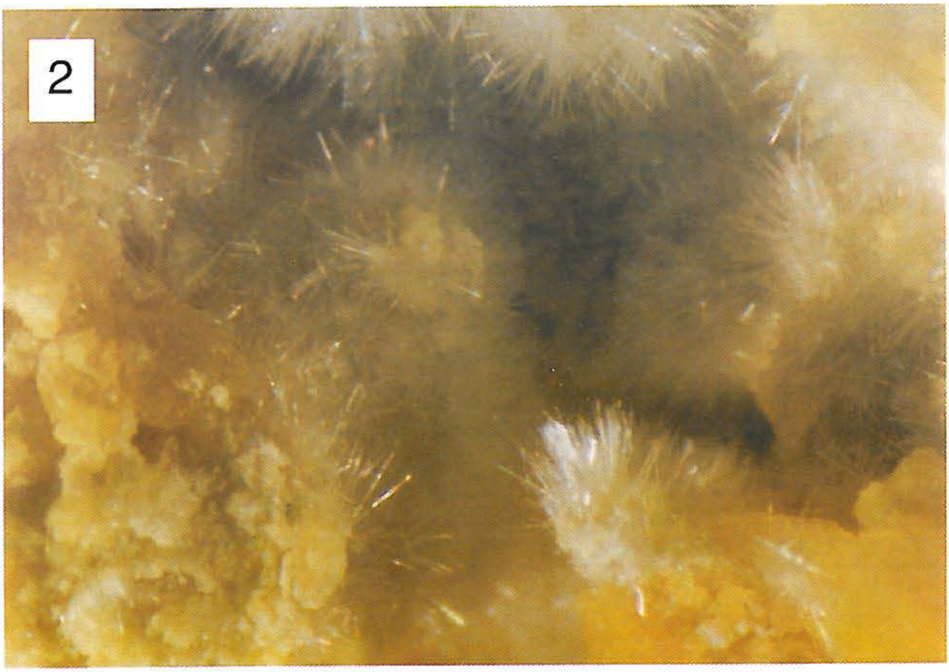
1 — Botryoidal aggregates of fibroferrite composed of fibrous crystals overgrowing each other, × 15

2 — Irregular aggregates of copiapite resembling in appearance and consistency native sulfur, × 10

1 — Botryoidal aggregates of copiapite crystallizing from semi-liquid masses creeping from the wall of the pit, × 10

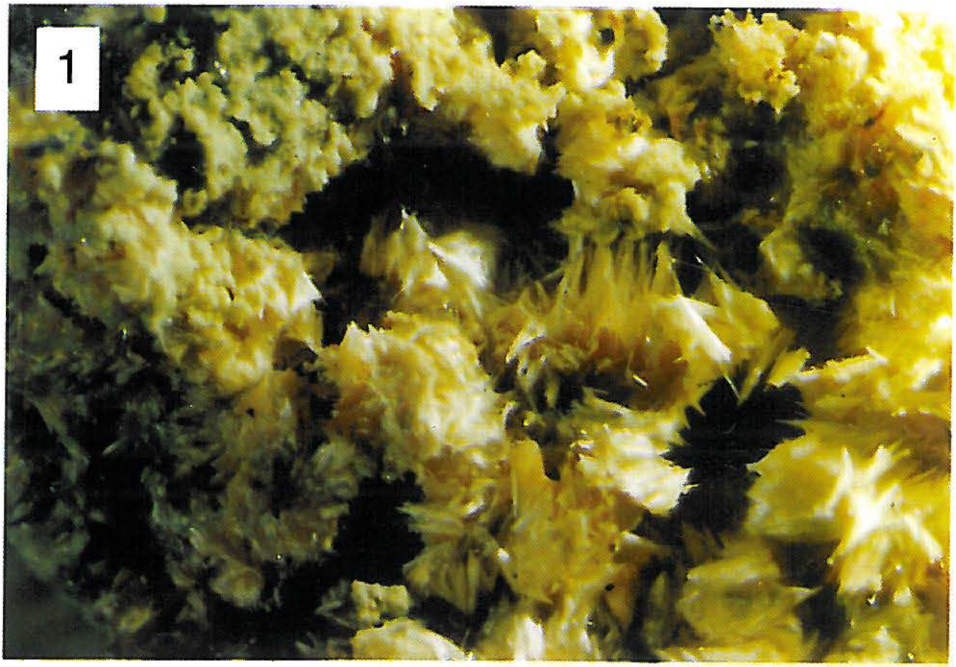
2 — Tabular gypsum crystals forming rosette incrustations, × 10





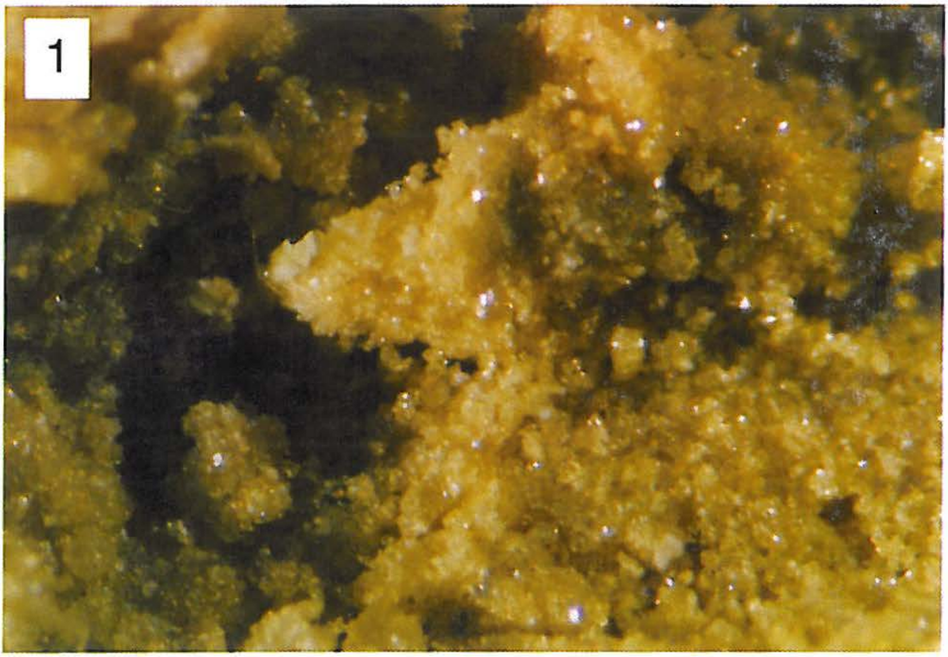
1 — Growths of fibrous pickeringite with silky luster, × 10

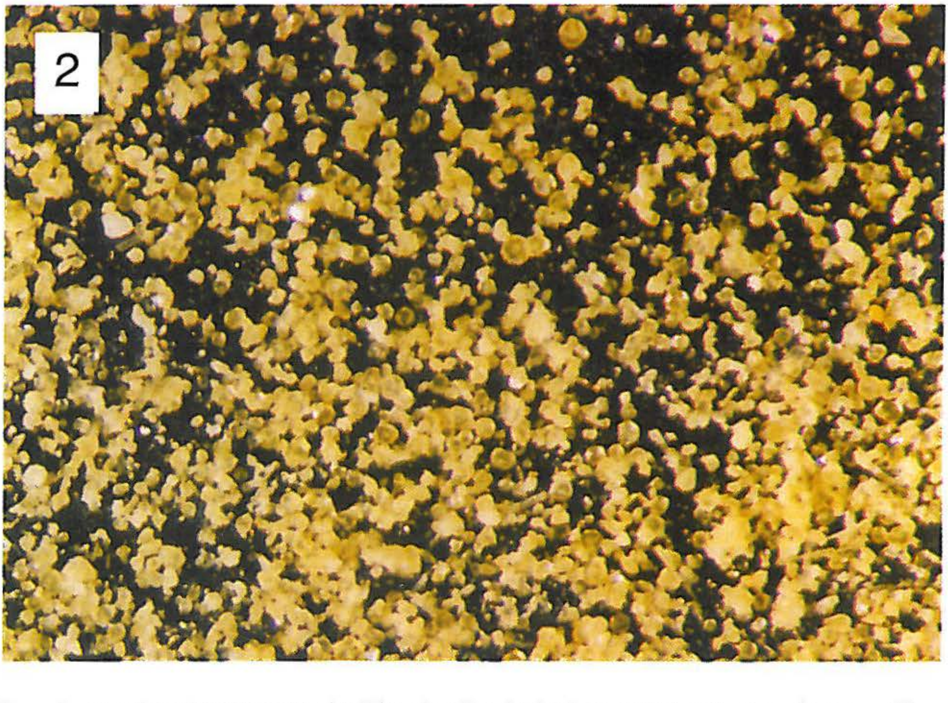
2 — Acicular pickeringite on yellow copiapite, × 15



1 — Ferric pickeringite of intensive yellow color, overgrowing copiapite, × 30

2 — Red-brown variety of fibroferrite; note pyrite grains (*one is arrowed*) preserved in sulfates, × 25





1 — Aggregates of saccharoid slavikite showing typical green tint and glassy luster, × 40

2 — Separate crystals of slavikite, some of which reveal trigonal symmetry and contain fluid inclusions; the biggest crystals are 0.03 mm in size ties. It is supposed to be a rare mineral, according to the VAN TASSEL's (1972) list, known only from about 20 locations in the world, half of them in Czech Republic and Slovakia. New studies suggest, however, that it is more common, though usually occurring in small amounts, component of weathering sulfate parageneses in temperate climatic zone.

The mineral name was introduced by JIRKOVSKÝ & URLICH (1926) to commemorate František SLAVIK (1876-1957), the professor of the Charles University in Prague. The same mineral was described earlier by KLVAŇ (1881) as paracoquimbite. According to the suggestion of ROST (1941), despite the priority rule, the latter name is currently used for the polymorphic variety of coquimbite, as proposed by UNGEMACH (1935). A mineral analogous to slavikite was named *franquenite* by VAN TASSEL (1944), who discredited later this name as an obsolete synonym.

Even a greater misunderstanding concerns the chemical formula of slavikite. Problems with separation of samples for chemical analysis that would be pure enough caused, that an appreciable part of the published analytical results bears significant errors. Consequently, this statement is pertinent to the chemical formulae, obtained from those analyses. The controversy sequence started from the publication of JIRKOVSKÝ & URLICH (1926) who discovered slavikite; they gave in the chemical analysis over 2% alkalis but they did not find magnesium. The chemical formula yielded from that analysis: $(Na,K)_2Fe_{10}[(OH)_6(SO_4)_{13}]\cdot 63H_2O$ one may find in the textbook by PALACHE & *al.* (1951). It caused doubts from the very beginning, sometimes leading to the neglect of this mineral species existence. Critical interpretation of the then obtainable data on slavikite, performed by ROST (1940), attributed the presence of alkalis to an admixture of jarosite, and presence of magnesium to an admixture of epsomite. As a consequence, the mineral encountered the group of the basic iron sulfates. The ROST's formula: $Fe[OH\ SO_4]\cdot 8H_2O$ is given in several older issues of the handbooks on descriptive mineralogy. Analyses of the relatively coarse-grained slavikite from Argentina, performed by GORDON (1941), resulted in ascertaining new formula of the mineral as a hydrous basic sulfate of iron and magnesium: $MgFe_3[(OH)_3(SO_4)_4]\cdot 18H_2O$, which was afterwards gradually accepted in handbooks and mineralogical lists. SUSSE (1975) on the basis of the studies of the mineral structure returned to the idea of alkali (sodium) presence in the composition of slavikite and proposed a new formula: $NaMg_2Fe_5[(OH)_6(SO_4)_7]\cdot 33H_2O$. Nevertheless, till present any proposed formula of slavikite is not commonly accepted.

The discovery of the new occurrence of slavikite at Wieściszowice may facilitate the solution of the mineral composition problem. The occurrence of slavikite in the form of macroscopically monomineral encrustations up to few centimeters thick may be especially favorable. Minerals of this type occur in pure state exceptionally and their complete separation from other sulfates is practically impossible. In samples from Wieściszowice one found in microscope few-percent admixtures of pickeringite and gypsum, however, any admixture of jarosite is absent, what is important to solve the problem of alkalis in the slavikite structure.

The results of the chemical analyses of slavikite (Table 4) indicate unambiguously, that alkalis are not any intrinsic component of this mineral, because none of the analyzed samples contain more than 0.02 % Na_2O

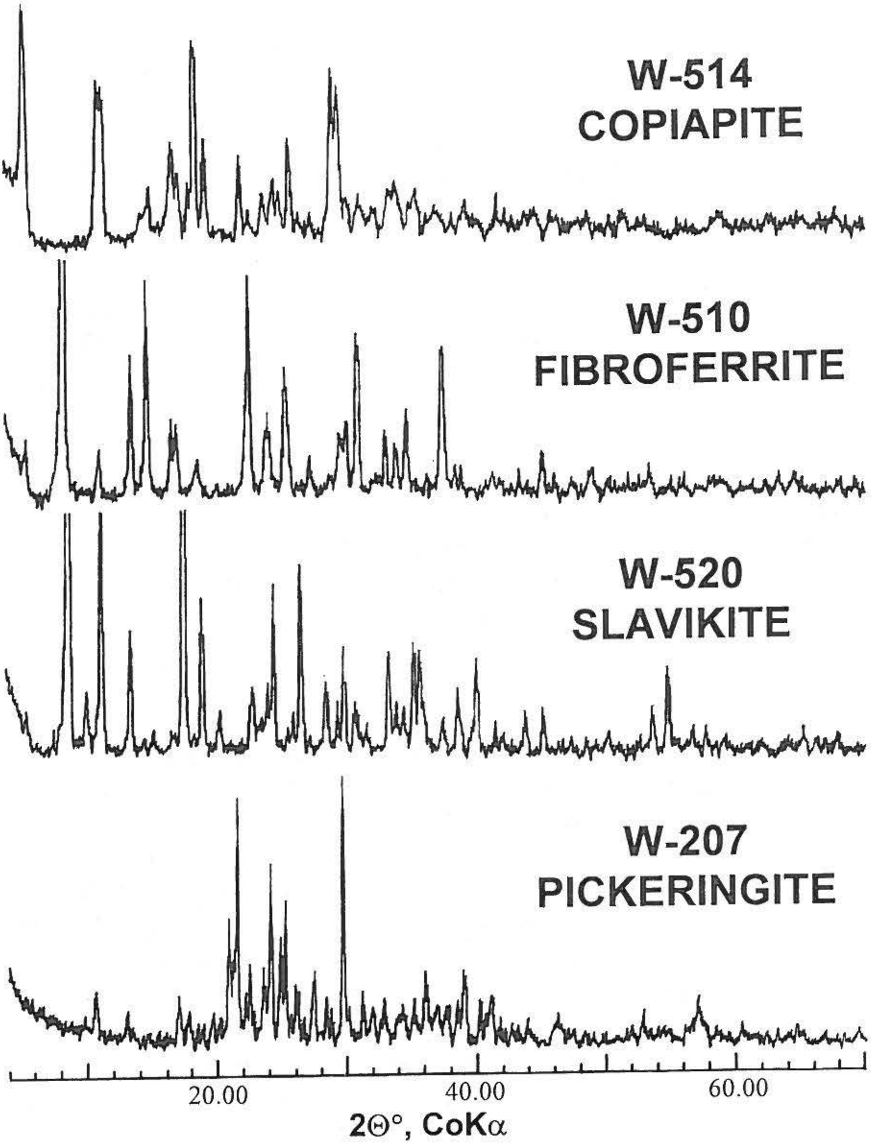


Fig. 6. X-ray powder patterns of separated samples of the sulfate minerals found at Wieściszowice

or K_2O. Thus, the mineral formulae proposed by Jirkovský & Urlich (1926) and by Susse (1975) are not to be confirmed. If one accepts the proposal of Makovický & Streško (1968) that aluminum in appreciable amount does not enter the slavikite structure, because samples of various

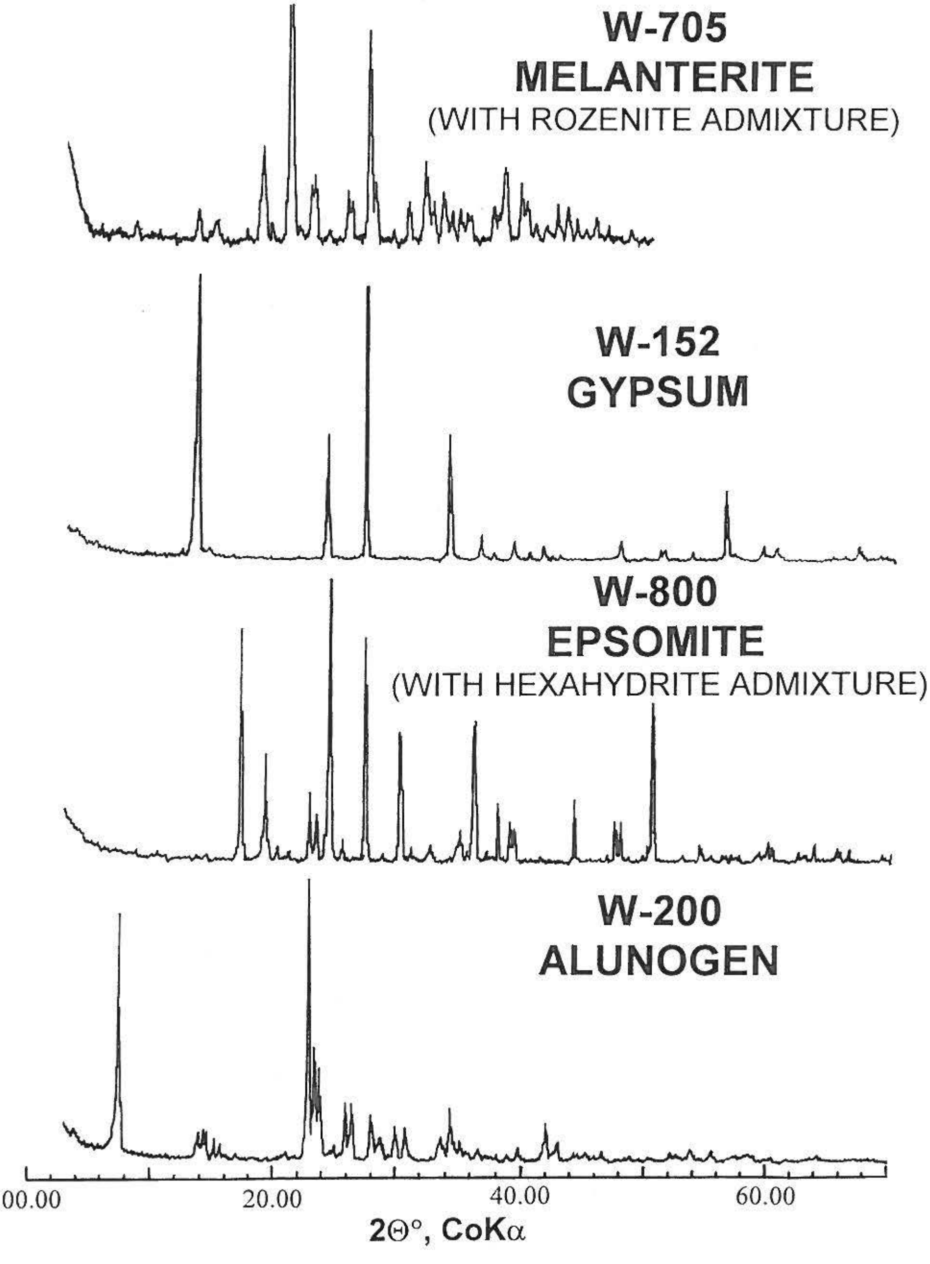


Table 4

Chemical composition of slavikite from Wieściszowice, wt.%

Sample	W-280	W-290	W-345	W-512	W-520	W-531
MgO	3.66	3.51	4.10	3.91	3.89	4.11
CaO	.18	.21	.14	1.45	2.14	.28
MnO	.02	.02	.02	.02	.04	.03
CuO	.01	.01	.00	.05	.03	.01
ZnO	.00	.00	.01	.00	.02	.01
Fe_2O_3	17.43	18.73	21.87	18.01	18.59	21.06
Al_2O_3	1.50	1.20	.45	1.14	1.01	.64
Na_2O	.01	.02	.01	.01	.02	.01
K_2O	.02	.02	.01	.00	.02	.01
SO_3	27.92	28.23	29.16	28.86	31.67	29.44
H_2O	31.77	31.33	34.34	35.88	36.67	38.87
insol.	12.37	11.57	10.16	11.16	7.27	8.43
total	94.87	94.85	100.27	100.49	101.37	102.90

Al_2O_3 contents display analogous optical features and X-ray diffraction parameters, thus the found contents of aluminum in the analyzed samples should be bound to an admixture of pickeringite. Similarly, the analytically found amount of calcium results from an admixture of gypsum in the slavikite samples. After introduction of the appropriate corrections, the analyses yielded a formula fitting very well to the GORDON's (1941) proposal: $MgFe_3[(OH)_3(SO_4)_4]\cdot 18H_2O$, which should be considered as the proper slavikite formula.

The content of the crystallization water in slavikite was determined on the basis of the thermogravimetric curve in the derivatograms. Thermic behavior of the mineral is close to other sulfates of similar chemical composition (IVANOVA & *al.* 1974). In the DTA curves one may distinguish five endothermic effects denoting the dehydration and dehydroxylation of slavikite, and two more endothermic effects of thermic decomposition of sulfates (Text-fig. 7). The first dehydration effect has its maximum at 100°C, the second – the strongest one at 130°C. The remaining three dehydration and dehydroxylation effects at 240°C, 400–420°C and 500–560°C are less distinct and sometimes masked by admixtures, e.g. pyrite. The composed character of the crystallization water release suggests, that the water occupies various positions in the mineral structure, being bound nonuniformly. The endothermic effect of the maximum at 700–720°C is caused by decomposition of iron sulfate and that at 900–920°C by decomposition of magnesium sulfate. All the endothermic effects are associated with the respective mass loss effects. One should mention that the slavikite samples, preserved under laboratory conditions for several years, did not display any sign of decomposition or alteration detectable by means of the X-ray diffraction.

Slavikite from Wieściszowice occurs in form of fine-crystalline encrustations (Pl. 8, Fig. 1). Crystals observed in microscope have the

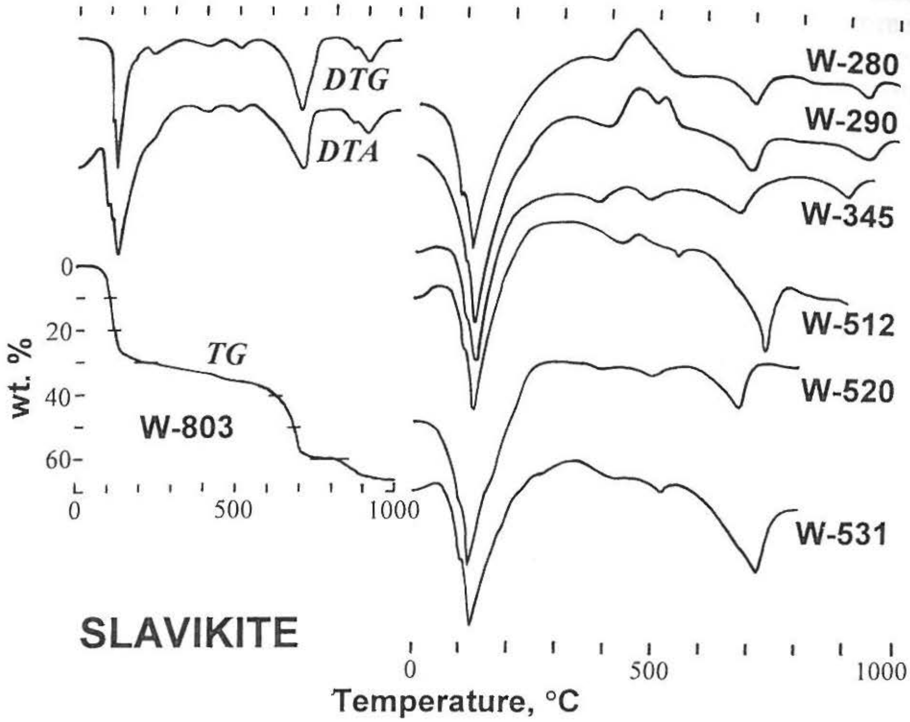


Fig. 7. An exemplary set of the derivatograms and DTA curves of slavikite

Run conditions: sample weight 300 mg, heating rate 10°C per min., DTA sensitivity 1/10, TG sensitivity 200

maximum size of 0.03 mm, but in average thousandth fractions of mm, what is typical of slavikite in many occurrences. Crystals are usually well-formed, they have tabular habit and reveal the trigonal symmetry (*see* Pl. 8, Fig. 2 and Pl. 13, Figs 1-3). They are flattened according to basal pinacoid and laterally rimmed by faces of one or occasionally few rhombohedrons. Relatively large crystals bear abundant fluid inclusions. Though macroscopically the slavikite accumulations are distinctly green, in microscope the mineral is yellow-greenish. The deep-green color and strong glassy luster allowed an easy field identification of slavikite in the sulfate paragenesis. Some crystals display a perfect cleavage according to (0001), not mentioned in the publications known to the present Author (Pl. 13, Fig. 4). The presence of this cleavage fits well to the layer structure model of slavikite (Text-fig. 8), proposed by SUSSE (1975). Layers parallel to (0001) and consisting of Fe-octahedrons and sulfate tetrahedrons arranged in six-fold rings, are the main structural feature of this mineral. The details of the slavikite structure are still to be refined, because the SUSSE's model was based on the incorrect chemical formula. Nevertheless, the values of the

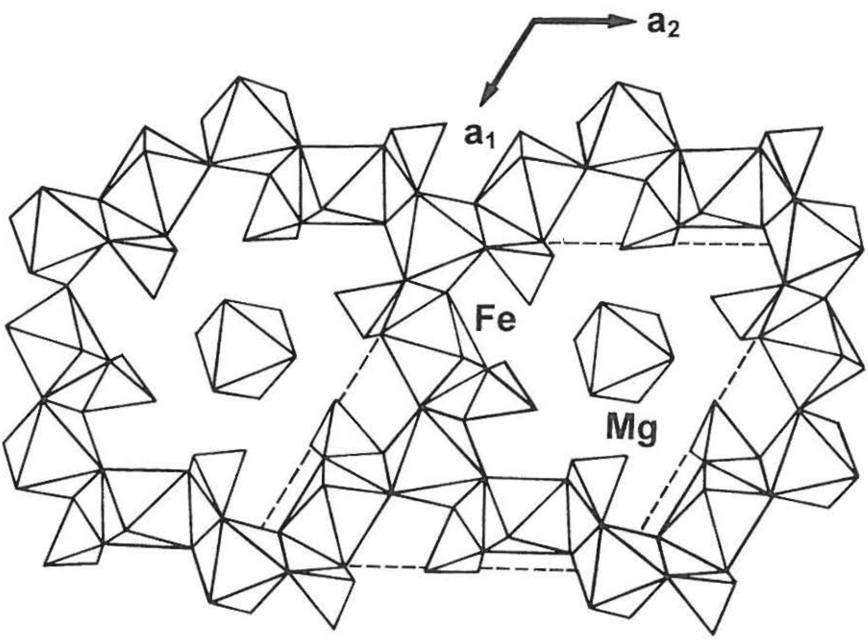


Fig. 8. Model of the slavikite structure (taken *from* SUSSE 1975)

unit cell parameters (a=12.17Å, c= 34.89Å) obtained in the present study are similar to the earlier published unit cell data of slavikite from Argentina: a=12.22Å, c=34.86Å (VAN TASSEL 1972); a=12.20Å, c=35.13Å (SUSSE 1975).

Slavikite is a mineral relatively resistant to the atmospheric factors in the described paragenesis. Its accumulations do not dissolve even in humid seasons of the year. Solubility of slavikite in water is comparable to that one of fibroferrite. Precipitation of slavikite seems to be determined mainly by chemical composition of the parent solutions, and to a lesser extent by solution concentration due to evaporation. It is possible to find large encrustations of pure slavikite at Wieściszowice, and achieving even almost half a meter in size, as well as its intergrowths with fibroferrite, sometimes also with pickeringite and copiapite.

Fibroferrite

Fibroferrite, belonging to the group of basic hydrous sulfates of iron III, was many times found in the weathering zones of sulfides, especially pyrite (CESBRON 1964, KOURIMSKÝ 1971, SABELLI & SANTUCCI 1987). It has a typical fibrous habit of the crystals, from which its name was derived. At Wieściszowice, similarly to the most of its known occurrences, the fibers of fibroferrite have fractions of mm in length and few micrometers in thickness (Pl. 3, Fig. 1). The fibrous habit is recognizable even macroscopically, because fibroferrite chips when rubbed with fingers, split into asbestos-like needles. Surface of flowstone, reniform aggregates display silky luster, typical of minerals of the fibrous habit (Pl. 3, Fig. 2; Pl. 4, Fig.1). The mineral color varies from silver-gray to olive-green, sometimes to yellowish and brownish tints and in rare cases to intensive red-brown (Pl. 7, Fig. 2). Fibroferrite is a common sulfate mineral of the described weathering zone. It covers the weathering pyrite-bearing schists as almost monomineral porous crusts of a surface of many square meters. Thickness of these crusts may exceed 1 cm.

The studies of this mineral performed till now indicate unambiguously the following chemical formula: $Fe[(OH)(SO_4)]\cdot 5H_2O$. Controversial is only the content of the crystallization water, whose amount ranges from 3 to 5 molecules per formula unit (p.f.u.), according to various authors, as listed by PALACHE & *al.* (1951). The results of the chemical analyses of the fibroferrite from Wieściszowice (Table 5) prove the presence of 5 water molecules p.f.u., similarly to the most of the recently published data. Chemical composition of this fibroferrite does not differ from the literature data. However, the admixtures of pickeringite, gypsum, and sometimes alunogen preclude the recognition which part of aluminum and calcium may be bound in the fibroferrite structure. Apparently aluminum in fibroferrite does not replace iron in any appreciable amount, but it is present as an admixture of foreign phases.

Results of crystallographic studies of fibroferrite are very variable. LARSEN (1921), BANDY (1938), and GORDON (1942) on the basis of the optic studies attributed it to orthorhombic symmetry (*vide* CÉSBRON 1964).

Table 5

Chemical composition of fibroferrite from Wieściszowice, wt.%

Sample	W-371	W-420	W-440	W-460	W-490	W-499	W-510
MgO	.53	.49	1.38	.68	.62	.46	.81
CaO	.34	1.21	.00	.99	.41	.76	2.35
MnO	.03	.02	.04	.03	.02	.02	.01
CuO	02	.01	.04	.04	.02	.02	.02
ZnO	.01	.04	.01	.01	.01	.04	.00
Fe_2O_3	24.40	27.40	22.06	24.37	25.68	26.67	25.35
Al_2O_3	.94	1.28	2.72	2.18	1.38	1.07	.59
SO_3	31.25	31.34	31.49	31.18	29.50	29.22	31.11
H_2O	33.33	36.45	35.00	37.97	35.57	35.33	37.81
insol.	4.23	.53	2.53	1.10	3.30	2.17	1.20
total	95.08	98.77	96.27	98.55	96.51	95.76	99.25

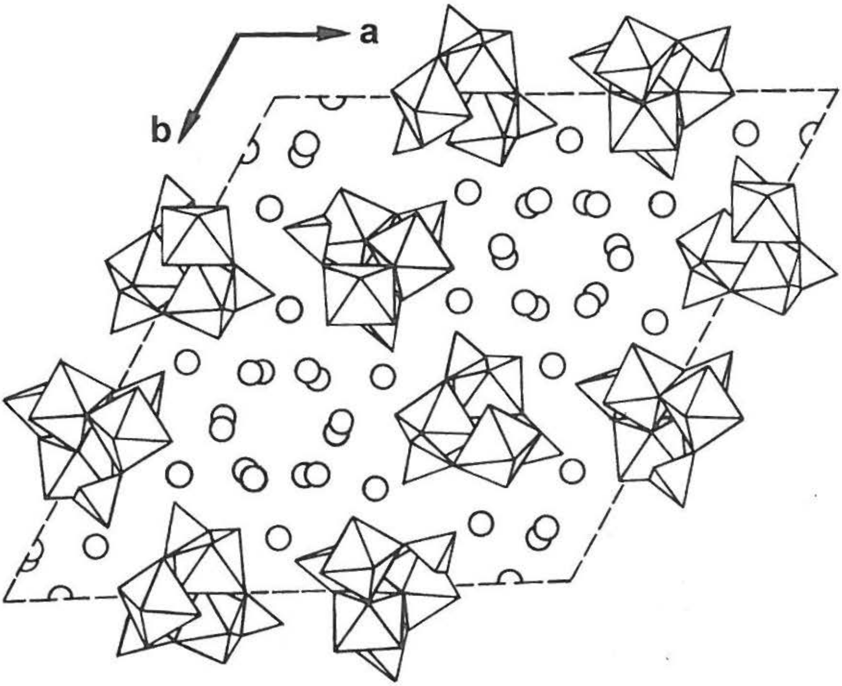


Fig. 9. Model of the fibroferrite structure (taken *from* SCORDARI 1981); circles show position of the crystallization water molecules

TOUSSAINT (1956) determined the symmetry by means of the X-ray studies as monoclinic with fibers elongated according to the *c*-axis. Finally CÉSBRON (1964) stated the trigonal symmetry of fibroferrite with a=24.12Å and c=7.63Å . The real symmetry is scarce visible on the crystal morphology. Commonly fibroferrite crystals reveal prismatic or lamellar habit (*see* Pl. 9, Figs 1-3). Afterwards, the CÉSBRON's data were confirmed by SCORDARI (1981): a=24.176Å, c=7.656Å. The structure, as elaborated by SCORDARI (1981), consists of spiral chains of Fe-octahedrons and sulfate tetrahedrons arranged along the *c*-axis (Text-fig. 9). The ion Fe III is surrounded by three water molecules, two hydroxyl groups, and 2 oxygen atoms shared with sulfate groups and located in the vertices of the octahedron. The remaining water molecules occur in the structural vacancies between the chains and are bound to them with weak hydrogen bonds. The positions of two crystallization water molecules are stabilized by four hydrogen bonds each, and that of the third water molecule by three hydrogen bonds.

The SCORDARI's model of the fibroferrite structure was confirmed by the results of the thermal studies of the mineral. The dehydration process recorded by the DTA and TG lines (Text-fig.10) consists at least of four stages, related to different energies of water linking in the mineral structure.

The first endothermic effect of dehydration has its maximum at *c*. 50–70°C. It is caused by a release of the molecule of the crystallization water, which is weakest linked in the structure. It is possible, that the dehydration may start at room temperature, as it was observed by CÉSBRON (1964). This would explain the variable hydration degree of fibroferrite reported in referenced papers. One should mention, however, that release of the first portion of water does not disturb the fibroferrite structure, because the X-ray powder patterns of the samples kept for several years under the laboratory conditions do not differ from that ones of the fresh samples. Release of the remaining crystallization water takes place in two stages at temperature intervals 120–150°C and 170–190°C. The first effect of the two ones is very distinct and dominates in the derivatogram, but the distinguishing of the second, high-temperature effect is difficult due to overlapping with the first one. Not rarely the both effects are recorded as one asymmetric endothermic peak. The fourth endothermic effect at 480–530°C is attributed to dehydroxylation. The distinct endothermic effect at *c*. 700–740°C is caused by thermal decomposition of iron sulfate; sometimes it is accompanied by smaller effects of thermal dissociation of aluminum and/or magnesium sulfate admixture. All the described thermal effects are associated with mass losses recorded by the TG lines (Text-fig. 10).

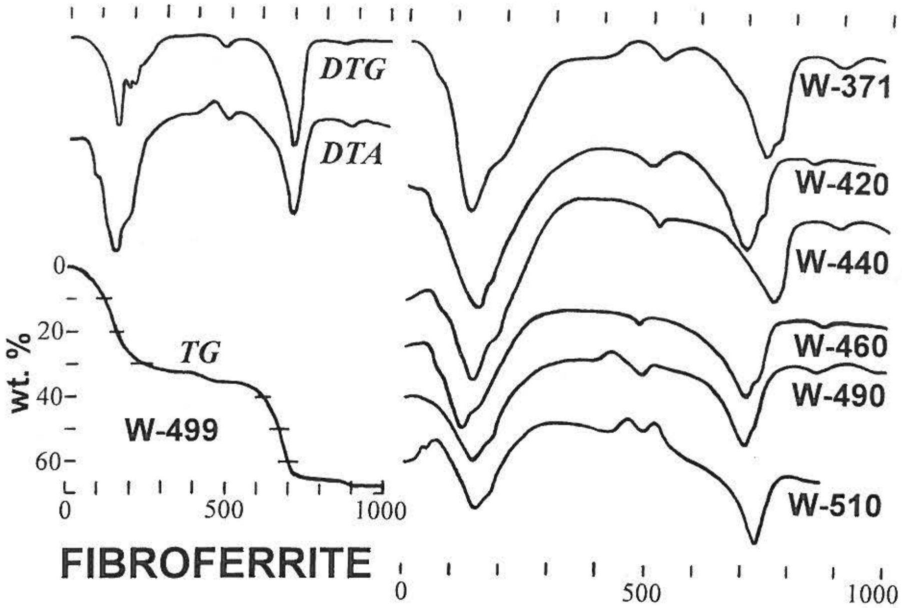


Fig. 10. An exemplary set of the derivatograms and DTA curves of fibroferrite; run conditions the same as given in Text-fig. 7

Fibroferrite is apparently a stable mineral, which does not display signs of alteration during keeping under room conditions during several years. In the samples of fibroferrite from Wieściszowice one did not observe any sign of alteration to parabutlerite, reported elsewhere by Césbron (1964).

Copiapite

The name of copiapite is usually applied for a group of minerals of a general formula: $A^{2+}Fe_4^{3+}[(OH)_2(SO_4)_6]\cdot 20H_2O$, where the A^{2+}-site may be occupied by Fe^{2+}, Mg, Zn, Cu, and Ca; another possibility is a formula $A^{3+}Fe_4^{3+}[(OH)_2O(SO_4)_6]\cdot 20H_2O$, where the A^{3+}-site is occupied by Al or Fe^{3+} (Fleischer 1983). However, the formula proposed by Bayliss & Atencio (1985): $A_{1-3x}^{2+}A_{2x}^{3+}\square_x Fe_4^{3+}[(OH)_2(SO_4)_6]\cdot 20H_2O$, probably is closer to the models of the structure and analyses of the chemical composition of this mineral group. It indicates, that the A-site may be completely occupied either by a bivalent cation (for $x=0$), or partly by a trivalent cation (up to the value of $x=1/3$), or within the limits determined by the formula simultaneously by bi- and trivalent metals.

Analyses of the natural samples indicate great possibilities of isomorphic replacements in the minerals of the copiapite group. Pure end members of this group are met occasionally in nature. Seven minerals of this group, including copiapite (where A-site is taken by ferrous iron), aluminocopiapite, magnesiocopiapite, ferricopiapite (A-site is taken by 0.66 ferric iron), zincocopiapite, cuprocopiapite and calciocopiapite are reported to occur in nature (Bandy 1938, Berry 1947, Kubisz 1964, Tu Kwang-chin & *al.* 1964, Jolly & Foster 1967, Fanfani & *al.* 1973, Perroud & *al.* 1987). They may be obtained relatively easily in laboratory experiments (Atencio 1994). Names of the mixed crystals are formed according to the Berry's (1947) proposal, on the basis of the cations occupying the A-site. Amount of the crystallization water molecules in the completely hydrated minerals is 20 (Fanfani & *al.* 1973); earlier Berry (1947) determined it on the basis of the accessible analyses as a statistical value of 20.7. Moreover, Wyszomirski (1992) described a uranium-bearing variety of copiapite from the kaolin deposit at Żarów, which contained 1.34% uranium and 0.44% cerium. Nevertheless, the problem whether the uranyl ion entered the copiapite structure or was adsorbed physically on the crystal surfaces, remained unsolved. For this reason, and due to great differences of the crystallochemical properties of the uranyl ion and cation components of copiapites, the uranium variety was not included to the present list. Additionally, by experimental mode the possibility of existence of mangano-, cobalt- and nickelcopiapite was shown (Atencio & Carvalho 1994), though they are unknown in nature.

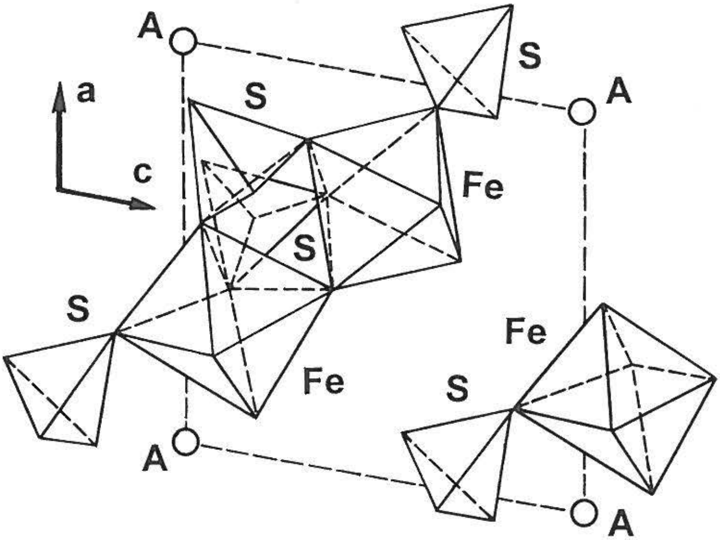


Fig. 11. Model of the copiapite structure (taken *from* SUSSE 1972)

All the minerals of the copiapite group are isostructural, as it is evidenced by their similar X-ray powder patterns and the unit cell parameters. In many cases the differenes among unit cell parameters of minerals belonging to the copiapite group are lesser than analytical errors. The model of the magnesiocopiapite, elaborated by SUSSE (1972), may be considered as a standard one for other varieties. In the copiapite structure there occur chains formed from pairs of the Fe octahedra linked linearly by the SO_4 tetrahedra. Other sulfate tetrahedra link the vertices of the octahedra in pairs, strengthening the bonds in the chains (Text-fig. 11). The chains are linked one to another only with the hydrogen bonds of the water molecules. These molecules are included in the isolated octahedra with cations in the A-sites as well as they occupy vacancies in the structure.

The exact identification of the copiapite group minerals on the basis of the X-ray diffraction powder patterns is frequently not sure. All these minerals have similar d_{hkl} values and only occasionally are discernible on the basis of the different reflection intensities. Moreover, the parameters of the unit cells of minerals in this group cannot be applied to the unambiguous identification, as it was shown by BAYLISS & ATENCIO (1985). Indexing of the powder X-ray diffraction data is also difficult due to large dimensions and the triclinic symmetry of the unit cells. For correct identification usually it is necessary to determine the chemical composition, though frequently the establishing of the right formula of the mineral is difficult even on the basis of the exact chemical analysis. This is caused by the fact, that copiapites always form fine-crystalline aggregates, and their thorough separation from possible admixtures of other weathering sulfates is practically impossible.

The results of chemical analyses of the selected samples of copiapite from Wieściszowice (Table 6) indicate, that magnesiocopiapite is the most common variety at this outcrop (*cf.* KUBISZ 1964). Magnesiocopiapite is a common mineral of the sulfate efflorescences, crystallizing on the surface

Table 6

Chemical composition of copiapite from Wieściszowice, wt.%

Sample	W-299	W-347	W-352	W-468	W-517	W-514	W-515
MgO	4.08	3.50	2.95	2.44	1.75	1.03	.83
CaO	.06	.06	1.45	.15	.12	.10	.10
MnO	.11	.08	.03	.04	.02	.02	.02
CuO	.01	.16	.01	.02	.05	.08	.12
ZnO	.01	.01	.01	.01	.02	.01	.01
FeO	1.06	.15	1.98	.20	.40	.40	1.14
Fe_2O_3	13.97	22.75	21.91	21.11	24.79	25.84	24.46
Al_2O_3	4.68	1.21	1.03	2.73	1.92	1.50	1.97
SO_3	36.91	36.11	37.00	37.54	37.66	37.05	37.44
H_2O	38.13	34.00	30.43	34.17	32.05	31.10	31.10
insol.	.10	.75	1.80	.50	.17	1.00	3.10
total	99.12	98.78	98.60	98.91	98.95	98.13	100.29
on the basis of 6 sulfur atoms							
Mg	1.33	1.16	.96	.78	.56	.33	.27
Ca	.01	.01	.34	.03	.03	.02	.02
Mn	.02	.01	.00	.01	.00	.00	.00
Cu	.00	.03	.00	.00	.01	.01	.02
Zn	.00	.00	.00	.00	.00	.00	.00
Fe^{2+}	.19	.03	.35	.03	.07	.07	.20
Fe^{3+}	2.27	3.78	3.55	3.38	3.95	4.18	3.93
Al	1.19	.31	.26	.68	.48	.38	.49
S	6	6	6	6	6	6	6
H_2O	25.54	23.11	19.93	22.28	20.69	20.39	20.14

Crystallographic formulae:

W-299: $(Mg_{1.33},Fe^{2+}_{0.19},Mn_{0.02},Ca_{0.01})Fe^{3+}_{2.27},Al_{1.19}[(OH)_2(SO_4)_6]\cdot 27.54H_2O$ (magnesiocopiapite with admixture of pickeringite)
W-347: $(Mg_{1.16},Al_{0.09},Fe^{2+}_{0.03},Cu_{0.03},Ca_{0.01},Mn_{0.01})Fe^{3+}_{3.78},Al_{0.22}[(OH)_2(SO_4)_6]\cdot 23.11H_2O$ (magnesiocopiapite)
W-352: $(Mg_{0.96},Fe^{2+}_{0.35},Ca_{0.34})Fe^{3+}_{3.55},Al_{0.26}[(OH)_2\ (SO_4)_6]\cdot 19.93H_2O$ (magnesiocopiapite)
W-468: $(Mg_{0.78},Al_{0.06},Fe^{2+}_{0.03},Ca_{0.03})Fe^{3+}_{3.38},Al_{0.32}[(OH)_2(SO_4)_6]\cdot 22.28H_2O$ (magnesiocopiapite)
W-517: $(Al_{0.43},Mg_{0.56},Fe^{2+}_{0.07},Ca_{0.03},Cu_{0.01})Fe^{3+}_{3.95},Al_{0.05}[(OH)_2(SO_4)_6]\cdot 20.69H_2O$ (alumino-magnesiocopiapite)
W-514: $(Al_{0.38},Mg_{0.33},Fe^{3+}_{0.18},Fe^{2+}_{0.07},Ca_{0.02},Cu_{0.01})Fe^{3+}_{4}[(OH)_2(SO_4)_6]\cdot 20.39H_2O$ (alumino-magnesiocopiapite)
W-515: $(Al_{0.42},Mg_{0.27},Fe^{2+}_{0.20},Ca_{0.02},Cu_{0.02})Fe^{3+}_{3.93},Al_{0.07}[(OH)_2(SO_4)_6]\cdot 20.14H_2O$ (aluminocopiapite)

of weathering pyrite-bearing schists, where it forms sulfur-yellow reniform accumulations (Pl. 4, Fig. 2 and Pl. 5, Fig. 1). They are commonly covered or intergrown with tiny pickeringite needles (Pl. 6, Fig. 2), not separable mechanically. The presence of this admixture of pickeringite, whose content is evaluate as equal few percent, influences the accuracy of the calculated chemical formula of the minerals. Certain copiapite samples may bear small admixtures of gypsum or epsomite. Despite the uncertainty caused by the pickeringite admixture, one may state that not all samples are magnesiocopiapite. The members, intermediate between magnesio- and aluminocopiapites are relatively frequent, up to almost pure aluminocopiapite (Table 6). A copiapite member with Fe II occupying up to 0.35 of the A-site was also found in three samples. The two latter varieties were unknown till present from the studied locality. The samples approaching aluminocopiapite were found at dumps. In the humid state they formed brown semi-liquid masses creeping from the walls of the pit in the dump. When dried, they became of the consistency and color typical of copiapite, except of ochreous tint sometimes present.

Copiapites belong to the most stable sulfate minerals that form in the acid environment of the sulfide weathering. Hence, they are common in the weathering zones. In the area of Poland they are known *e.g.* from the Zn-Pb mine Bolesław (ŻABIŃSKI 1960), Dobrzyń-on-Vistula River (MAZUR 1962), Rudki near Nowa Słupia (WIESER 1949), Turoszów (STĘPISIEWICZ 1983), and Borów near Strzegom (AUGUST 1984). Their occurrence is limited by their very good solubility in water, thus the characteristic yellow efflorescences of copiapite may be found only in sheltered places, or during long periods without rainy weather. Reniform accumulations of copiapite consist of tabular crystals not discernible with a naked eye, grouped in parallel or fan-like aggregates. The crystals are usually few micrometers in size and they reveal its triclinic symmetry only in microscope image (Pl. 10, Figs 1-3).

Thermal decomposition of copiapite is complicated. All the studied samples display a large endothermic effect at 700–730°C caused by thermal dissociation of iron sulfate. The samples bearing appreciable amounts of magnesium or aluminum yield also effects of dissociation of the respective sulfates. Copiapite dehydration takes place at least in five stages, commonly overlapping one another and sometimes difficult to separate. The DTA curve record endothermic peaks at 100–120°C, 140–160°C, 180–190°C, 320–350°C and 480–500°C (Text-fig. 12). This indicates a differentiated energy of water linking, that display various role in the copiapite structure. It fits well to the structure proposed by SUSSE (1972), in which of 20 water molecules p.f.u., 8 molecules are linked to Fe III, and 6 are coordinated with the A-site cation occupying the vertices of the octahedron, and the remain-

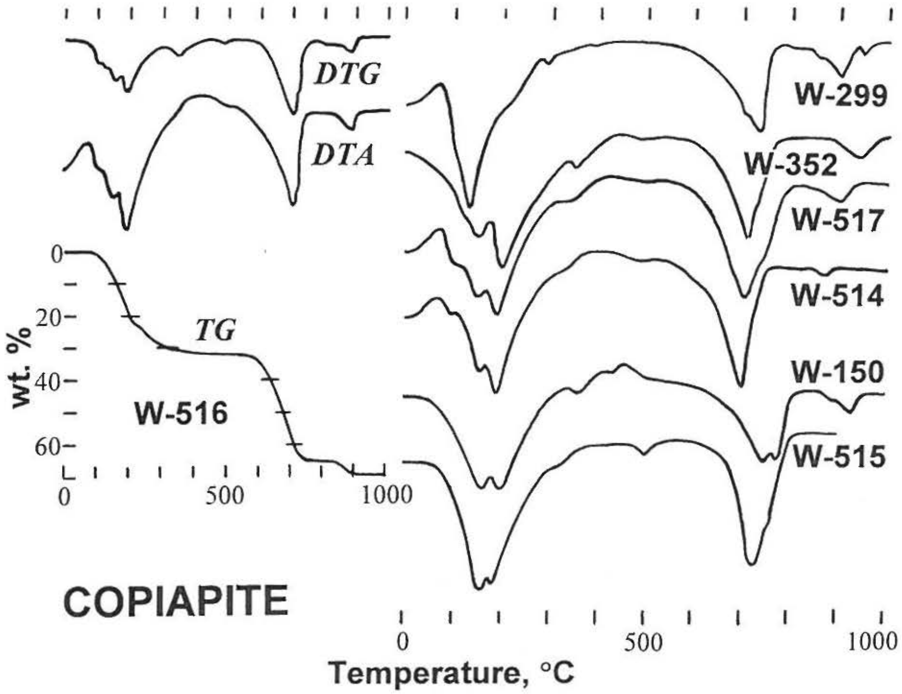


Fig. 12. An exemplary set of the derivatograms and DTA curves of copiapite; run conditions the same as given in Text-fig. 7

ing 6 molecules are linked to the structure only with hydrogen bonds. It is worth noting the differences between the DTA curves, of copiapite with a bivalent metal (mainly magnesium) in the A-site, and of that one bearing a trivalent metal (aluminum) in the same site. Apparently they are discernible in the basis of the most intensive dehydration peaks. Copiapite bearing a bivalent metal produces the highest peak at 180–190°C, whereas that with a trivalent metal yields the highest peak at 140–160°C. This observation should be verified with use of pure end members of the copiapite group, and, if confirmed, could be used as a convenient identification feature.

Pickeringite

Minerals of the halotrichite group, especially the most common halotrichite and pickeringite, frequently occur in the weathering zones of sulfides, particularly pyrite. They are also widespread in volcanic exhalation products. These minerals form small acicular or fibrous crystals of length rarely exceeding 1 mm. The terminating parts of the crystals are euhedral only in exceptional cases (Pl. 12, Fig. 1; Pl. 14, Fig. 2). Fluffy, subtle efflorescences, overgrowing either the surfaces of the weathering rocks or other sulfates, are the typical form of these minerals (Pl. 11, Fig. 1-2; Pl. 12, Fig. 2). Occasionally they also form growths of silky luster (Pl. 6, Fig. 1). Usually these minerals are colorless or white, but that bear Mn or Fe III are respectively pale pink or yellow.

There are many analogies of the halotrichite and copiapite groups. Minerals of the halotrichite group display various isomorphic replacements, what causes common formation of natural mixed crystals. The general formula of the halotrichite group is given as follows: $Me^{2+}Me^{3+}_2[SO_4]_4 \cdot 22H_2O$, where $Me^{2+} = Fe^{2+}$, Mg, Mn and Zn, Me^{3+} =Al, Fe^{3+} and Cr. Minerals to be found in nature include following end-members: $FeAl_2[SO_4]_4 \cdot 22H_2O$ (halotrichite), $MgAl_2[SO_4]_4 \cdot 22H_2O$ (pickeringite), $MnAl_2[SO_4]_4 \cdot 22H_2O$ (apjohnite), $ZnAl_2[SO_4]_4 \cdot 22H_2O$ (dietrichite), $FeFe_2[SO_4]_4 \cdot 22H_2O$ (bilinite), and $FeCr_2[SO_4]_4 \cdot 22H_2O$ (redingtonite). Names of the mixed crystals, like those of copiapites, are formed taking into account the prevailing cation. Minerals of the composition strictly corresponding to the theoretical end-member formulae occur rarely in nature, but mixed crystals are commonly found. On the basis of the published chemical analyses one may state the existence of the continuous mixed crystal series halotrichite–pickeringite. Miscibility occurs also between the two latter minerals and apjohnite (*see e.g.* GARAVELLI 1955), and probably between all the end-members of the group.

KUBISZ (1964) found halotrichite in a sample from Wieściszowice on the basis of the X-ray powder pattern. The present Author's studies did not confirm this statement, but they showed, that another mineral of the same group, *viz*. pickeringite is a common component of the weathering zone at Wieściszowice. These two minerals yield similar X-ray powder patterns, and they may be mistaken one for another during a routine diffraction analysis, like other minerals of the halotrichite group. An exact identification requires usually chemical analyses. Difficulties in identification may explain the fact, that pickeringite from Wieściszowice is the first described finding of this mineral in Poland (PARAFINIUK 1991), though halotrichte was noted many times (WIESER 1949, MAZUR 1962). The present Author supposes, that pickeringite is distinctly more common than it appears from the published records, as it is suggested by its following finding at Krobica (PARAFINIUK 1994).

The collected chemical analyses of pickeringite from Wieściszowice (Table 7) indicate, that at this location there occur members close to pure pickeringite. None of the studied samples had halotrichite composition, since Fe II occupied up to 13% of the Me^{2+} site in the mineral structure. The MnO contents do not exceed 0.5 wt.%, thus the apjohnite end-member content is very low. Although the studied pickeringite samples bore lit-

Table 7

Chemical composition of pickeringite from Wieściszowice, wt.%

Sample	W-370	W-387	W-423	W-555	W-402	W-361	W-401
MgO	5.48	5.58	3.63	4.12	4.50	3.98	5.03
CaO	.03	.05	.05	.07	.07	.08	.20
MnO	.31	.49	.43	.39	.32	.31	.30
CuO	.00	.04	.07	.23	.11	.24	.18
ZnO	.03	.03	.02	.09	.02	.03	.03
FeO	.05	.72	.00	.30	.60	.79	1.04
Fe_2O_3	.00	.73	3.99	5.75	6.30	6.75	7.28
Al_2O_3	9.19	9.65	10.77	8.91	7.49	8.14	5.92
SO_3	31.94	35.93	36.20	35.69	35.67	34.44	34.17
H_2O	52.16	46.00	45.15	43.77	44.22	42.67	41.06
insol.	.70	.00	.00	.00	.58	.37	4.08
total	99.90	99.22	100.31	99.32	99.88	97.80	99.29
on the basis of 4 sulfur atoms							
Mg	1.37	1.24	.80	.92	1.01	.92	1.18
Ca	.00	.01	.01	.01	.01	.01	.03
Mn	.04	.06	.05	.05	.04	.04	.03
Cu	.00	.00	.01	.02	.01	.03	.02
Zn	.00	.00	.00	.01	.00	.00	.00
Fe^{2+}	.01	.09	.00	.04	.07	.10	.13
Fe^{3+}	.00	.08	.44	.64	.71	.78	.85
Al	1.95	1.69	1.87	1.56	1.32	1.48	1.09
S	4	4	4	4	4	4	4
H_2O	29.04	22.76	22.24	21.81	22.04	22.03	21.36

Crystallographic formulae:

W-370: $(Mg_{1.37},Mn_{0.04},Fe^{2+}{}_{0.01})Al_{1.95}[SO_4]_4\cdot 29.04H_2O$
W-387: $(Mg_{1.24},Fe^{2+}{}_{0.09},Mn_{0.06},Ca_{0.01})Al_{1.69},Fe^{3+}{}_{0.08}[SO_4]_4\cdot 22.76H_2O$
W-423: $(Mg_{0.80},Mn_{0.05},Cu_{0.01},Ca_{0.01})Al_{1.87},Fe^{3+}{}_{0.44}[SO_4]_4\cdot 22.24H_2O$
W-555: $(Mg_{0.92},Mn_{0.05},Fe^{2+}{}_{0.04},Cu_{0.02},Zn_{0.01},Ca_{0.01})Al_{1.56},Fe^{3+}{}_{0.64}[SO_4]_4\cdot 21.81H_2O$
W-402: $(Mg_{1.01},Fe^{2+}{}_{0.07},Mn_{0.04},Cu_{0.01},Ca_{0.01})Al_{1.32},Fe^{3+}{}_{0.71}[SO_4]_4\cdot 22.04H_2O$
W-361: $(Mg_{0.92},Fe^{2+}{}_{0.10},Mn_{0.04},Cu_{0.03},Ca_{0.01})Al_{1.48},Fe^{3+}{}_{0.78}[SO_4]_4\cdot 22.03H_2O$
W-401: $(Mg_{1.18},Fe^{2+}{}_{0.13},Mn_{0.03},Ca_{0.03},Cu_{0.02})Al_{1.09},Fe^{3+}{}_{0.85}[SO_4]_4\cdot 21.36H_2O$

tle Fe II, some of them contain appreciable amounts of Fe III, what consequently led to recognition of a new variety of this mineral, unknown till present. The published analyses of pickeringite showed usually a minor substitution of aluminum by trivalent iron. Any mineral of the formula $MgFe^{3+}{}_2[SO_4]_4\cdot 22H_2O$, which would be a magnesium analogue of bilinite, is not recently known, though reasons excluding its existence are difficult to find. Contrary, its presence would complete by natural mode the possible isomorphism in this mineral group according to the scheme:

$$\begin{tikzcd}
\begin{array}{c} FeAl_2[SO_4]_4\cdot 22H_2O \\ \text{halotrichite} \end{array} \arrow[r, leftrightarrow] \arrow[d, leftrightarrow] & \begin{array}{c} MgAl_2[SO_4]_4\cdot 22H_2O \\ \text{pickeringite} \end{array} \arrow[d, leftrightarrow] \\
\begin{array}{c} FeFe_2[SO_4]_4\cdot 22H_2O \\ \text{bilinite} \end{array} \arrow[r, leftrightarrow] & \begin{array}{c} MgFe_2[SO_4]_4\cdot 22H_2O \\ \text{supposed end-member} \end{array}
\end{tikzcd}$$

The studies of the sulfate minerals from Wieściszowice performed do not give any sufficient basis to distinguish this hypothetical mineral. Samples with iron III prevailing over aluminum, a possible pickeringite variety that would be recognized as a new mineral, were not found. Nevertheless, the performed analyses indicate, that the substitution Al–Fe III in the halotrichite group is fairly more extensive that it was supposed earlier. The study results suggest miscibility between pickeringite and the new hypothetical end-member $MgFe_2[SO_4]_4\cdot 22H_2O$ at least to the Al:Fe III ratio equal *c.* 1:1. This variety should be named ferric pickeringite, to distinguish from ferrous pickeringite, the variety bearing an admixture of halotrichite molecule.

The Fe^{3+}-rich variety of pickeringite may be distinguished macroscopically on the basis of its color: they are creamy, yellow, light brown of various tints, whereas pure pickeringite is white (Pl. 7, Fig. 1). Wet Fe^{3+}-rich variety is much darker than dry one, having even chocolate color, which gradually changes to pale-brown and yellow on drying. Similar yellowish color is typical of bilinite, which also bears ferric iron.

Extensive possibilities of isomorphism in the minerals of the halotrichite group are to be explained by similarity of their structures. Detailed studies of the structure were formerly performed only for apjohnite (Menchetti & Sabelli 1976), however, the same structure pattern may be apparently applied to other minerals of the halotrichite group. This is indicated by great similarities of the powder diffraction data and very close unit cell parameters, as follows (in Å, except as indicated):

apjohnite (Menchetti & Sabelli 1976)	a = 6.198 b = 24.347 c = 21.267 β = 100.28°
halotrichite (Lovas 1986)	a = 6.195 b = 24.262 c = 21.262 β = 100.30°
pickeringite (*this paper*)	a = 6.150 b = 24.154 c = 21.234 β = 100.53°

The parameters of the unit cell of pickeringite from Wieściszowice, determined on the basis of the X-ray powder pattern does not depend significantly on the isomorphic replacement of Al by Fe III.

In the mineral structure the octahedrons $Me^{3+}(H_2O)_6$ and $Me^{2+}O(OH)_5$ and the tetrahedrons SO_4 are linked almost exclusively by the hydrogen bond system. Only one sulfate tetrahedron joints the octahedron

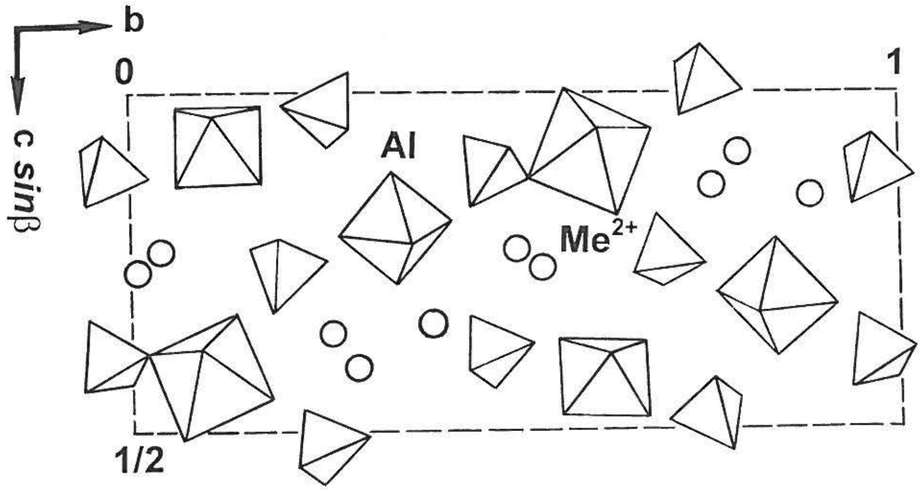


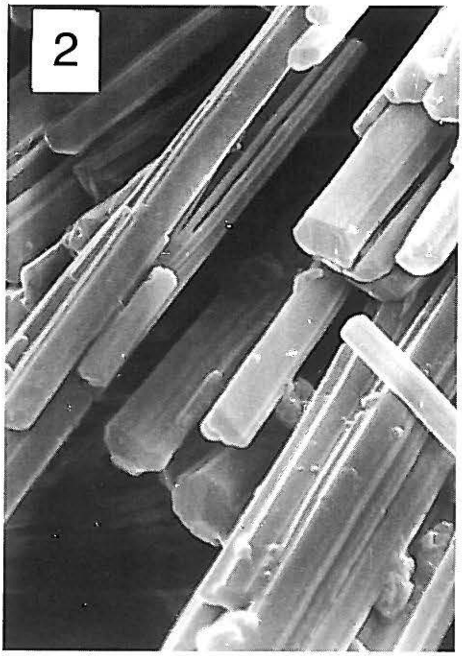
Fig. 13. Model of the apjohnite structure (taken *from* MENCHETTI & SABELLI 1976)

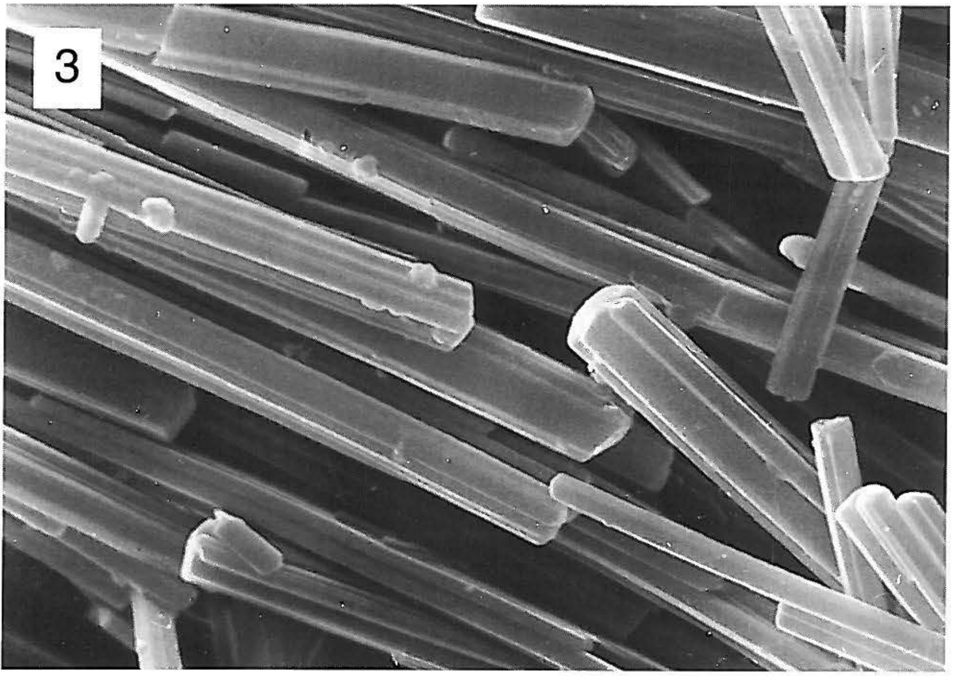
of bivalent metal through a common oxygen atom (Text-fig. 13). Five water molecules are not bound to cations but they are stabilized by hydrogen bonds and they occupy the structural vacancies.

The described model of the structure was confirmed by the results of the thermal analysis (Text-fig. 14). Dehydration of the minerals is easy and occurs in several stages. Most of the water molecules is released in the first two stages, recorded by the endothermic peaks at 100 and 120°C. The DTA curves show the dehydration effects also at 290–320°C and 400–420°C. Moreover, the effects of desulfurisation are present at 700–740°C (decomposition of aluminum and iron sulfates) and at 870–900°C (magnesium sulfate decomposition). Unlike copiapite and fibroferrite, the low-temperature desulfurisation effect is recorded as a single peak. The increase of iron content in the pickeringite structure causes decrease of temperature of this effect. However, thermal analysis is not appropriate to distinguish the individual mineral varieties and it is only of supplementary importance.

Other sulfate minerals

Gypsum is a common sulfate mineral in the described weathering zone. Its fine tabular crystals associate almost all the minerals of the paragenesis (Pl. 5, Fig. 2; Pl.14, Fig. 3). Locally gypsum covers surfaces of the weathering schists of many square meters as a few-millimeter thick crust of dome-shaped radial aggregates. Gypsum is easy for macroscopic identification due to characteristic habit of the crystals. The aggregates are

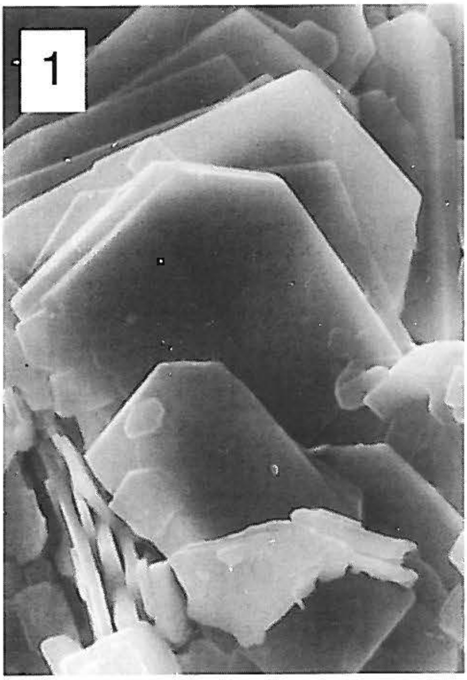


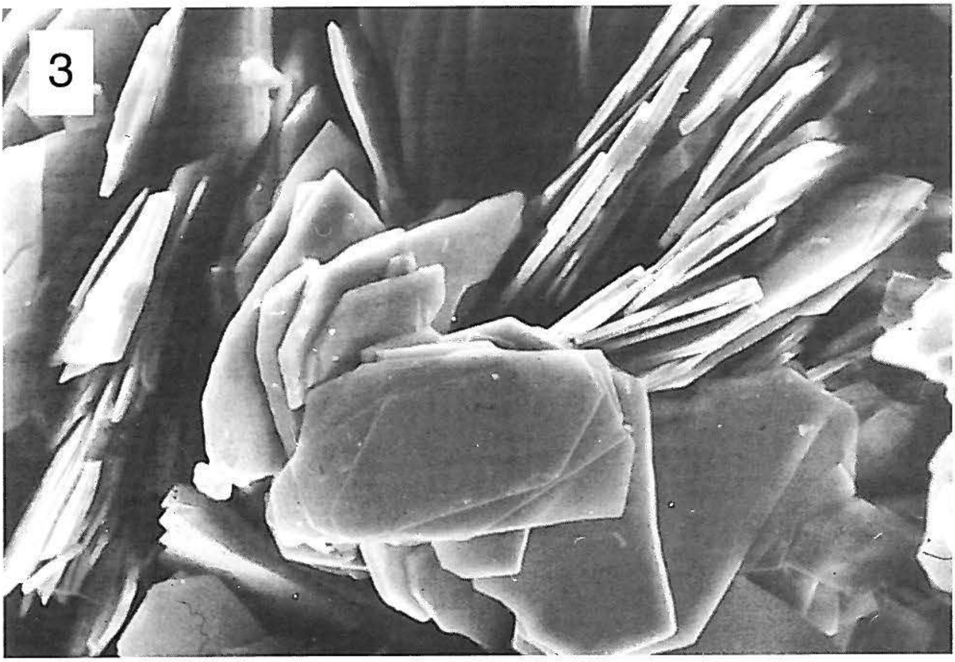


1 — Acicular fibroferrite crystals grouped into parallel or fan-like aggregates; SEM, × 900

2 — Terminated prismatic fibroferrite crystals, some of which reveal trigonal symmetry; SEM, × 2000

3 — Flattened prisms of fibroferrite, to show its typical habit at Wieściszowice; SEM, × 1900

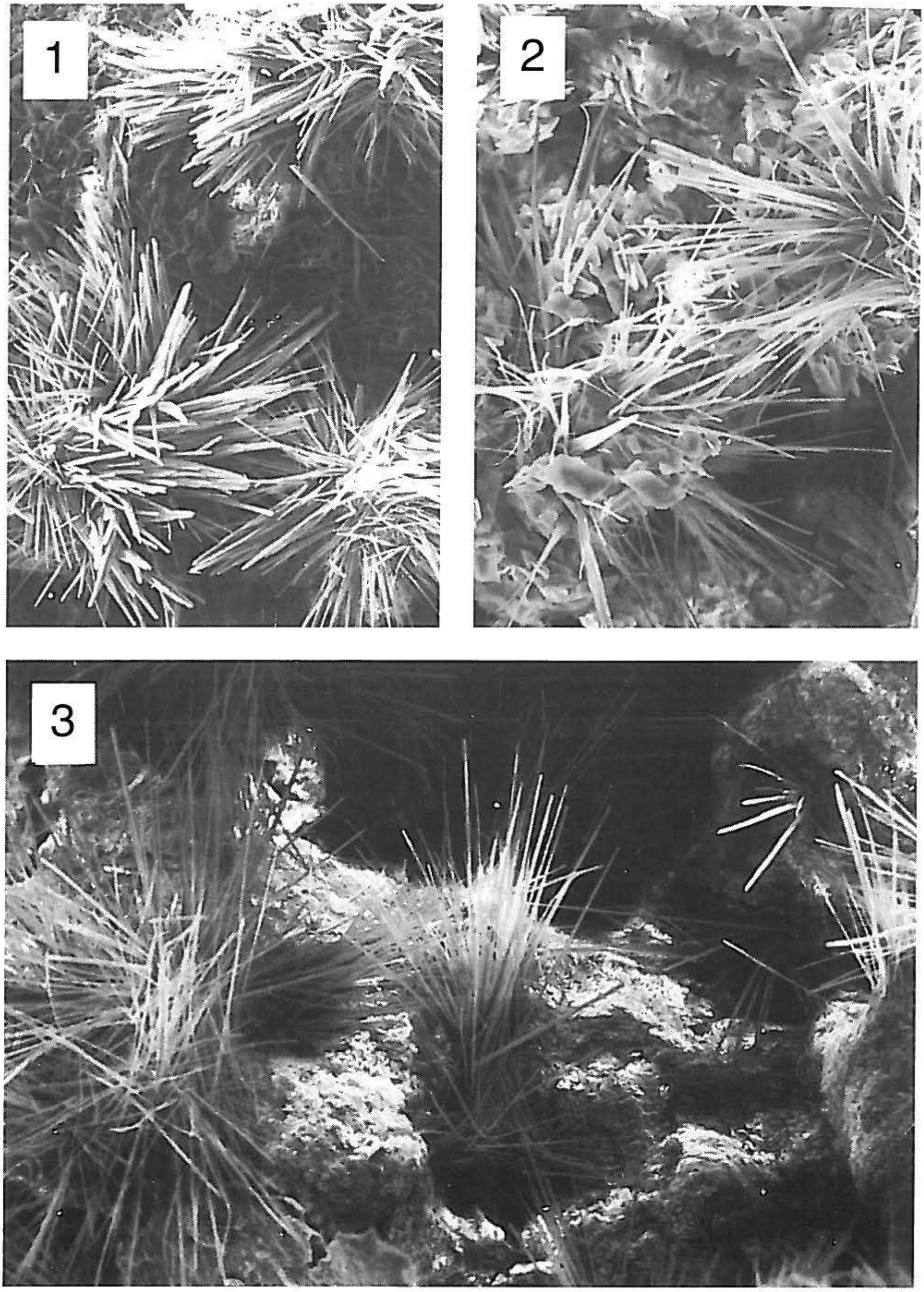




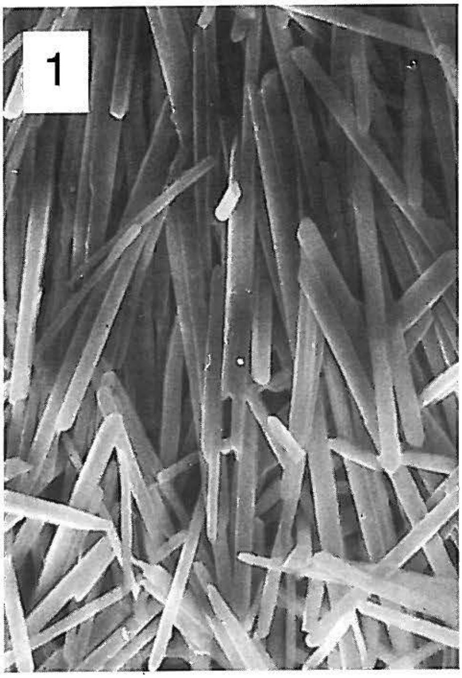
1 — Euhedral crystals of copiapite showing tabular habit and triclinic symmetry; SEM, × 2300

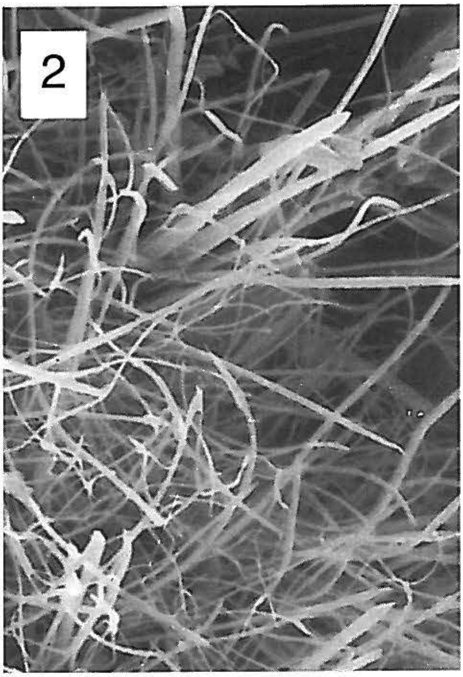
2 — Plates of copiapite, plastically deformed; SEM, × 2400

3 — Tabular copiapite crystals grouped in parallel or fan-like aggregates; SEM, × 1800



1-2 — Acicular pickeringite on copiapite; SEM, × 200
3 — Bunches of pickeringite needles on the schist surface; SEM, × 150

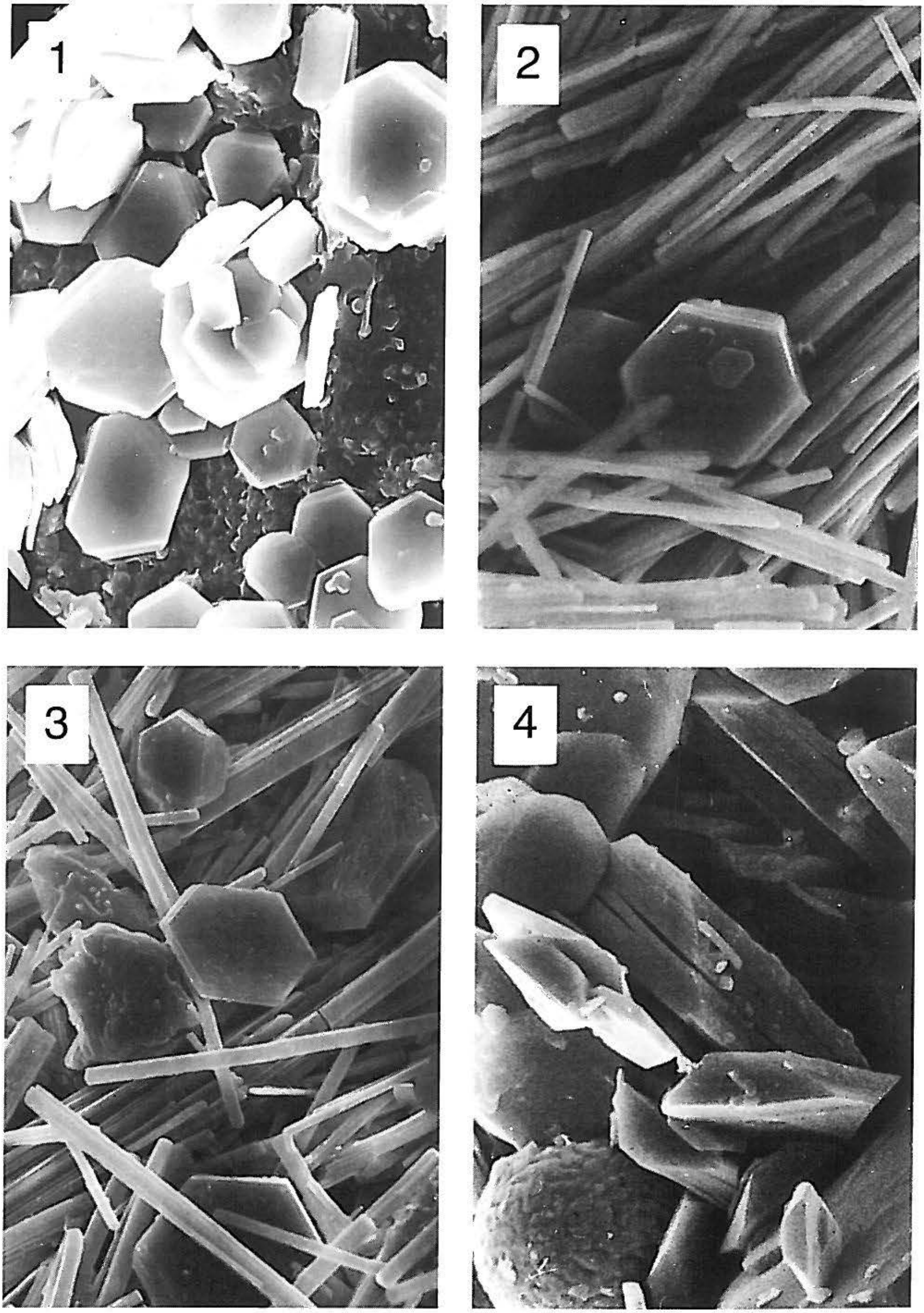




1 — Prismatic pickeringite crystals; SEM, × 500

2 — Fluffy, hair-like variety of pickeringite; SEM, × 100

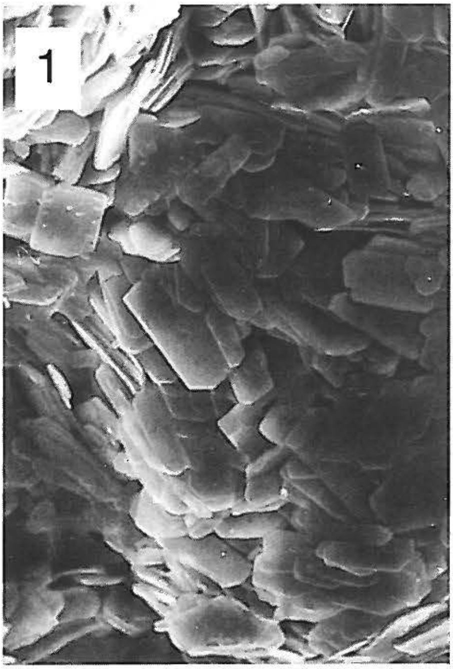
3 — Efflorescences of hairy, twisted epsomite crystals; SEM, × 250

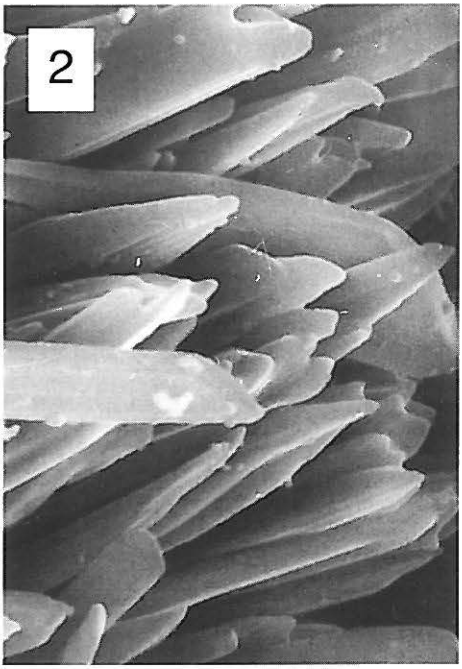


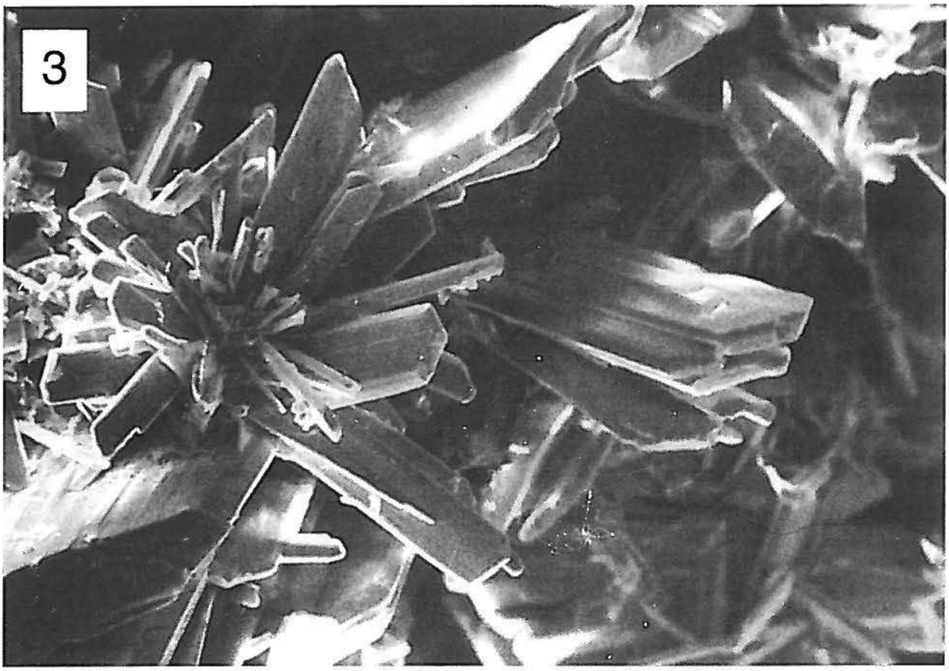
1 — Tabular slavikite crystals with distinct trigonal symmetry growing on the schist surface; SEM, × 2000

2-3 — Euhedral slavikite plates in aggregates of fibroferrite; SEM, × 3000

4 — Slavikite crystals with perfect cleavage planes parallel to basal pinacoid; SEM, × 4000







1 — Globular aggregate composed of tabular copiapite; SEM, × 900

2 — Poorly terminated prisms of pickeringite; SEM, × 2500

3 — Rosettes of gypsum crystals amongst the sulfate minerals; SEM, × 200

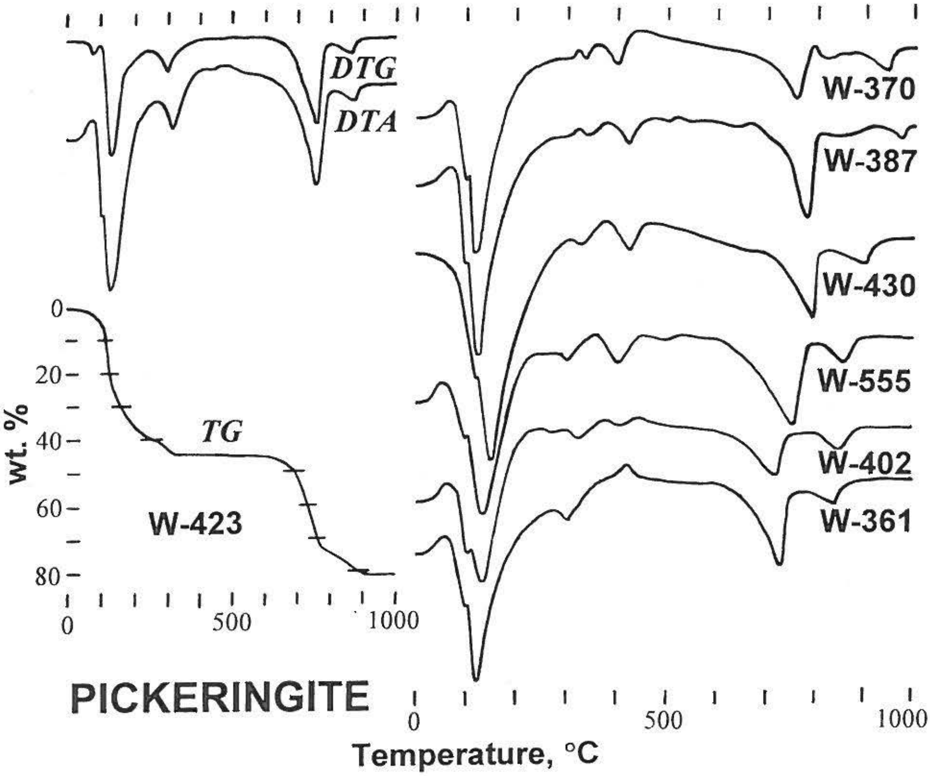


Fig. 14. An exemplary set of the derivatograms and DTA curves of pickeringite; run conditions the same as given in Text-fig. 7

white or grayish because of mechanic admixtures, rarely colorless and transparent.

Melanterite $FeSO_4 \cdot 7H_2O$ is known only from one finding at Wieściszowice, thus is apparently a rare mineral there. It was found on an isolated rock of pyrite-bearing schist, where it formed fine-grained few-millimeter-thick encrustation of white-greenish color. It occurred as a single sulfate, not associated with other ones, although the X-ray powder pattern revealed the presence of subordinate rozenite $FeSO_4 \cdot 4H_2O$ which, however, could be the product of melanterite dehydration, possibly in laboratory. The latter is the stable phase under room conditions (JAMBOR & TRAILL 1963).

Epsomite $MgSO_4 \cdot 7H_2O$ may be frequently found on the surface of the schists after prolonged periods of dry weather in form of small, millimeter-sized white fluffy efflorescences of hairy, twisted crystals (Pl. 12, Fig. 3). Usually it accompanies more abundant pickeringite. Epsomite was also met in the dumps as a cement of the ground schist particles. Under room conditions this mineral is unstable like melanterite and alters into hexahydrite $MgSO_4 \cdot 6H_2O$, as evidenced by X-ray powder patterns.

Alunogen $Al_2[SO_4]_3 \cdot 18H_2O$ is relatively rare and found occasionally. It occurs in periods of low-humidity weather as a minor admixture of the fibroferrite and pickeringite aggregates. Its fine, grainy, sugar-like colorless or white aggregates are discernible only under a microscope. Tabular flat crystals up to 1 mm in size are exceptional.

Heavy metals in sulfates

Chemical analyses (Table 8) show, that appreciable amounts of heavy metals, released from weathering pyrite and host rocks, entered the newly-

Table 8

Minor elements in sulfate minerals from Wieściszowice (in wt.% × 0.001)

Sample	Mn	Cu	Zn	Co	Ni	V	Cr	Pb
Pickeringite								
W-401	233	141	24	15	6	5	1	<1
W-402	249	91	20	14	5	2	1	<1
W-370	242	4	18	14	8	<1	1	7
W-387	379	32	24	18	5	<1	<1	<1
W-423	334	54	21	14	3	1	1	2
W-555	301	180	75	16	9	2	1	1
W-361	240	189	24	12	6	3	1	1
Copiapite								
W-514	13	67	9	7	5	1	5	2
W-515	16	95	11	8	7	3	4	8
W-517	14	43	15	6	5	1	6	2
W-299	86	9	11	6	6	1	8	1
W-468	31	18	9	5	2	<1	1	2
W-352	22	9	5	4	3	2	1	7
W-347	59	126	10	9	2	<1	1	5
W-390	73	14	10	5	6	1	8	5
Fibroferrite								
W-371	22	17	5	3	1	<1	1	5
W-510	8	19	5	2	1	<1	1	5
W-383	17	15	5	2	1	<1	1	6
W-420	14	5	36	2	<1	1	<1	2
W-440	32	32	6	4	<1	1	<1	2
W-460	26	35	5	2	<1	1	<1	1
W-490	14	14	11	2	<1	1	1	2
W-499	16	16	33	1	<1	1	<1	2
Slavikite								
W-280	17	11	4	2	<1	<1	<1	<1
W-290	16	1	1	1	1	<1	1	<1
W-345	13	<1	6	4	1	<1	<1	4
W-512	27	53	4	4	2	1	1	6
W-520	33	22	17	5	3	<1	3	4
W-531	21	6	9	7	3	<1	2	4

formed sulfates. Hence, the sulfates are an important agent of retention of these environmentally toxic components. Thus, crystallization and dissolution of the sulfate minerals control to a significant extent the concentrations of heavy metals in the weathering zone. A wide variation of the heavy metal concentrations was stated in the studied minerals. This differentiation is mainly caused by local changes of heavy metal concentrations in pyrite and weathering minerals of the schist. The geochemical affinity of these metals to the main cations of the sulfate minerals, especially to iron and to a lesser extent to aluminum and magnesium, is an important factor. Apparently, in many cases the open type of the structure is essential for inclusion of appreciable amounts of isomorphic admixtures.

The highest manganese concentrations amounting to tenths percent, was found in pickeringite. They exceed at least ten times the manganese concentrations in copiapite, fibroferrite and slavikite. So high contents are caused by good fitting of manganese to the pickeringite-type structure, what is evidenced by the manganese mineral species of apjohnite, isostructural with pickeringite. Tenths percent copper was found in pickeringite and copiapite, what may be caused by existence of cuprocopiapite, though copper analogue of halotrichite is unknown. The copper contents display large scattering down to the values lower than 0.001wt.%. The highest zinc concentrations of hundredths percent occur in pickeringite, but copiapite contains distinctly less zinc, although zinc analogues of both minerals exist. Similarly high concentrations of zinc were detected in certain samples of fibroferrite and slavikite, though the average content in these minerals is much lower.

Cobalt achieves more than one hundredth percent in pickeringite, up to this value in copiapite and few thousandths percent in fibroferrite and slavikite. Nickel enters the structures of the studied minerals in amounts lesser than cobalt: thousandths percent in copiapite and pickeringite and even less than 0.001wt.% in fibroferrite and slavikite. Concentrations of vanadium and chromium amount usually *c.* 0.001wt.% or less, only copiapite bears few thousandths wt.% chromium, and pickeringite similar content of vanadium. Several thousandths percent lead were found in copiapite and fibroferrite, whereas pickeringite commonly contains less than 0.001wt.%. Other heavy metals enter the mineral structures in amounts lower than 0.001wt.%.

The heavy metal contents, although display distinct variations in the studied parageneses, are not suitable to explain the origin of the studied minerals. One may suppose, that concentrations of the most of the metals in the parent solutions of the sulfate minerals were lower than those determined from the partition coefficients solution/crystal. The differences resulted, in addition to the structural factor, from local, variable concentrations of the solutions. Apparently, the heavy metal concentrations are distinctly higher in highly soluble minerals like pickeringite and copiapite, which crystallized from more concentrated solutions.

ISOTOPE COMPOSITION OF THE SULFATES

SULFUR

The ratios of the sulfur isotopes in weathering sulfates has hitherto been presented only in some publications. This is apparently caused by a common opinion, that during sulfide oxidation to sulfates any distinct isotope fractionation does not occur. If compared to the isotope fractionation effect, resulting from the bacterial reduction of sulfate to hydrogen sulfide, the isotope signature of the sulfide oxidation is in fact much weaker and frequently ambiguous. Nevertheless, a series of reports on physical experiments, attempt the determination of numeric values of the sulfur fractionation during sulfide oxidation (*see* KAPLAN & RITTENBERG 1964, NAKAI & JENSEN 1964, LEWIS & KROUSE 1969, TAYLOR & *al.* 1984, FRY & *al.* 1988).

It seems, that generally the sulfates formed from oxidized sulfides have the sulfur isotopic composition slightly lighter that the parent sulfide. This fractionation is more distinct for dissolved sulfide achieving -18‰ for aerobic oxidation of H_2S by *Thiobacillus concretivorous* as stated by KAPLAN & RITTENBERG (1964), and -5.2‰ for non-biological oxidation of sulfide (FRY & *al.* 1988) than for parent solid, *e.g.* pyrite, for which as a rule it does not exceed +0.1‰ (TAYLOR & *al.* 1984). In the case of a sulfide mineral the sulfur isotope fractionation in the oxidation process is so insignificant, that the sulfur isotope composition may be used as the genetic index for sulfates. It is difficult to ascertain the relation between the sulfur fractionation and the mechanism of sulfide oxidation. Both inorganic and bacterial oxidation may yield similar isotopic effects although FRY & *al.* (1988) stated, that bacterial oxidation in the aerobic environment causes a decrease, while in anaerobic environment an increase of ^{34}S content in sulfate.

Isotope composition of the sulfate mineral products of the pyrite oxidation has rarely been determined. The literature supplies the examples of both enrichment of gypsum and jarosite in the isotope ^{34}S of the value of 7–10‰ if compared to the parent pyrite (NISSENBAUM & RAFTER 1967), and impoverishment these minerals of the value of 4–8‰ (GRINENKO & GRINENKO 1975). These isotope data, so different from experimental results, may suggest, that other processes of isotope fractionation than solely oxidation influenced the final product in the quoted studies, *e.g.* bacterial sulfate reduction.

The weathering zone of the pyrite-bearing schists at Wieściszowice is a convenient object of model isotope studies in temperate climate. The homogeneous sulfur isotope composition of pyrite is an important factor, facilitating an interpretation of the results obtained.

Separated fresh (without visible signs of weathering) pyrite crystals from Wieściszowice yield the $\delta^{34}S$ values from 1.0 to 2.2‰ (mean value of 6 analyses is 1.6‰). This determination is necessary not only for estimation of the isotope effect of weathering, but also it is useful to the genetic considerations on the pyrite deposit. Although this latter context is not of the main interest of the present Author, seemingly the sulfur isotope ratio in pyrite may be the crucial evidence in the discussion on the sedimentary versus hydrothermal origin of the mineralization. Homogeneous isotope composition of the pyrite in the deposit, close to the troilite standard excludes sedimentary origin, because sedimentary sulfides bear usually lighter sulfur of large $\delta^{34}S$ value variation (OHMOTO & RYE 1979, NIELSEN 1985). Thus, the hypothesis of the deep-seated source of sulfur and hydrothermal formation of the deposit is reasonable. In the present Author's opinion, the genesis of the deposit is best explained by JASKÓLSKI (1964), who linked its formation with activity of seawater on the submarine basaltic lava effusions, although the sulfur source must be involved other, than marine sulfates suggested by JASKÓLSKI.

Comparison of the sulfur isotope composition of pyrite and weathering sulfate minerals (Table 9) confirm a small fractionation of sulfur isotopes during pyrite oxidation. If one accepts, that sulfates from the Purple Pond water represent an average isotope composition of the products of the pyrite weathering, transported from the altered schists, it appears that their sulfur has the isotope composition like the parent pyrite. The sulfur isotope composition of the weathering sulfates might be influenced by external contamination, and atmospheric precipitation (acid rains) may be the main source of the foreign sulfur. Sulfate concentrations from 9 to 13 mg per liter were found in rain water in the neighboring area of the Jelenia Góra Valley (HRYNIEWICZ & PRZYBYLSKA 1993), which may be pertinent to the region under study as well. In comparison with the sulfate concentrations in waters of the weathering zone, the input from atmospheric contamination is negligible low. Isotope studies of the precipitation in the area under study were not performed till present. The average $\delta^{34}S$ value of sulfates in rain water, determined for the Lublin area in eastern Poland, is *c.* 3.3‰ (TREMBACZOWSKI 1991), being very close to the average value of the atmospheric sulfates (KROUSE 1980). Thus, the isotope composition of the atmospheric sulfates does not contrast with that of the weathering ones in the Wieściszowice area. Thus, the atmospheric sulfur does not influence in recognizable degree the isotopic composition of the sulfates at Wieściszowice.

Small, but worth noting sulfur isotope fractionation was observed between individual mineral species at Wieściszowice (Text-fig. 15). Gypsum has the isotopically heaviest sulfur (mean $\delta^{34}S$ = 2.7‰). Fibroferrite is also enriched in the ^{34}S isotope (mean $\delta^{34}S$ = 2.3‰), if compared to pyrite. Other studied sulfates are slightly poorer in this isotope than pyrite. The mean $\delta^{34}S$ for copiapite and pickeringite equals

Table 9

Sulfur and oxygen isotopic composition in sulfate minerals from Wieściszowice

Sample	$\delta^{34}S_{CDT}$,‰	$\delta^{18}O_{SMOW}$,‰
Gypsum		
W-102	3.1	-4.5
W-103	2.6	-4.1
W-105	3.3	-2.9
W-106	3.1	-2.6
W-152	2.3	-3.3
W-250	1.7	-4.9
Fibroferrite		
W-114	1.9	-3.2
W-122	2.7	-4.2
W-151	1.7	-3.1
W-154	2.6	-3.0
W-251	2.5	-1.5
Copiapite		
W-111	1.1	-5.7
W-150	1.3	-1.6
W-161	1.8	-3.9
W-167	1.1	-5.3
W-204	1.9	-5.4
W-215	0.3	-2.6
W-217	2.0	-1.6
Pickeringite		
W-112	1.7	-5.0
W-125	2.1	-3.9
W-127	0.9	-5.5
W-202	1.9	-3.6
W-207	0.9	-6.2
W-210	1.0	-4.1
W-220	1.4	-4.2
Epsomite		
W-153	1.4	-5.5
W-164	0.3	-4.5
W-166	0.5	-4.7
Sulfate ion in the Purple Pond		
W-131	1.1	-1.1
W-132	2.2	-4.6
W-133	2.2	-5.6

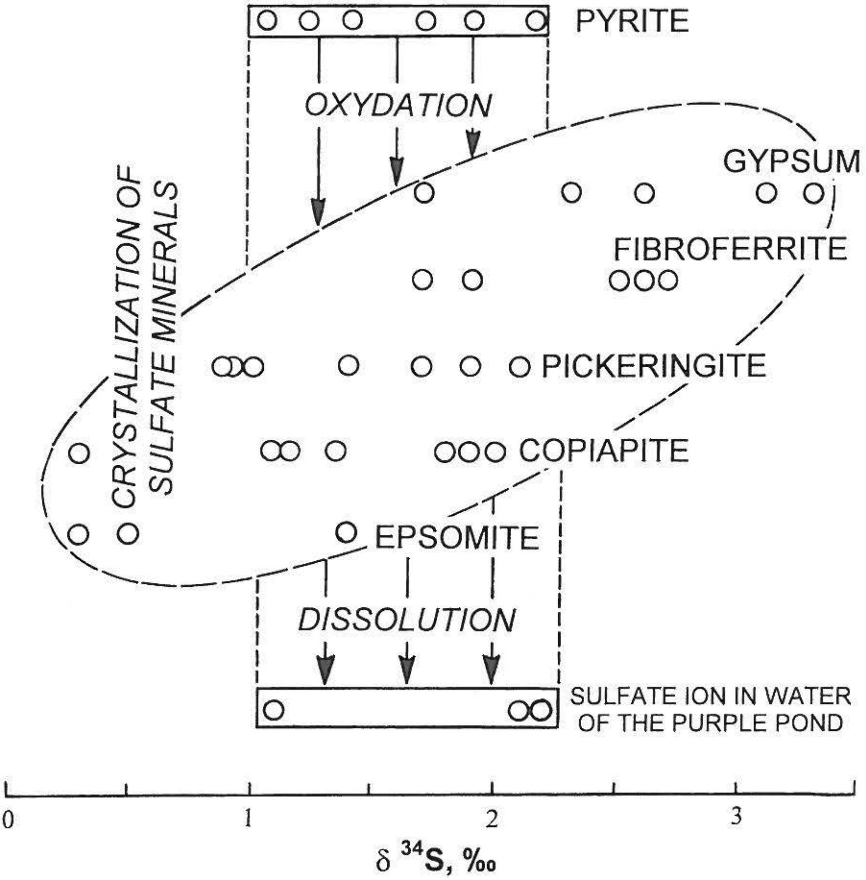


Fig. 15. Sulfur isotope composition of sulfate minerals from Wieściszowice

c. 1.4‰, and for epsomite even 0.7‰, the lightest sulfur isotope composition found in the studied sulfates.

The found changes cannot be interpreted as an effect of the fractionation, associated with pyrite oxidation. The sulfate minerals do not form directly from the parent pyrite. Rather, the determined isotope fractionation is connected with sulfate crystallization from solution. This is strongly suggested by the dependence of the sulfur isotope composition on the mineral solubility in water (*see* Text-fig. 15): the poorer solubility of a mineral, the richer it is in heavy isotope. This tendency should be confirmed by experimental determination of isotope fractionation coefficients for the crystallization of sulfates. Till present fractionation coefficient is known only for gypsum amounting +1.65‰ (THODE & MONSTER 1965).

Enrichment of the early sulfates in crystallization sequence in $\delta^{34}S$ isotope is apparently a common phenomenon. A similar effect was observed during seawater evaporation (RAAB & SPIRO 1991), when during an experimental run the $\delta^{34}S$ values for gypsum gradually decreased from 21.92‰ at the stage of the early sulfate crystallization to 19.09‰ at the final stage of halite facies. Gypsum crystals were always enriched in ^{34}S with respect to the parent solutions according to the fractionation ratio, determined for this mineral. Similar tendencies were observed for sulfate minerals of the Zechstein evaporates from Germany (NIELSEN & RICKE 1964).

OXYGEN

Isotope composition of oxygen in weathering sulfates was considered as an genetic index in the past, especially useful to studies of the sulfide-to-sulfate oxidation (Taylor & al. 1984). On this basis one attempted to determine quantitatively sources oxygen fixed in the sulfate ions (atmosphere, water molecules of the reacting solution). Because the isotopic exchange of oxygen bound in the sulfate molecule, with oxygen from atmosphere or water at low temperature is extremely low, the genetic record coded in the isotope composition, under the condition of contamination absence, may be preserved safely. More detailed discussion of this problem will be presented later.

Analyses of the isotope composition of oxygen in sulfate minerals from Wieściszowice (Table 9) were performed for all the samples analyzed for sulfur isotopes. The $\delta^{18}O$ values for sulfates vary from -1.1 to -6.2‰; somewhat broader than for sulfur isotopes. Any significant correlation of the isotope composition of sulfur and that one of oxygen was not observed in the studied minerals. Also relationships between oxygen isotope composition and mineral species are absent. Similar $\delta^{18}O$ values (-2.1 to -6.1‰) in mine outflow water and sulfate efflorescences on pyrite-bearing schists in the Bohemian massif was found by ŠMEJKAL (1979). Such values seem to be typical of weathering sulfates formed in temperate climate conditions.

Crystallization water

Distinctly lower binding energy of crystallization water in the sulfate structure, when compared with binding energy of oxygen in sulfate ions causes, that isotope exchange of oxygen (and hydrogen) in crystallization water takes place distinctly easier than in the SO_4^{2-} ions. Thus, the studies of the isotope composition of water from hydrated sulfates may be considered as a good tool of determination of the conditions of formation and stability of the discussed minerals.

Isotope studies of crystallization water were performed for samples of gypsum, fibroferrite, copiapite, and pickeringite, collected systematically every month of the year 1991 (Parafiniuk 1997). Isotope composition of crystallization water of the sulfate minerals was afterwards compared with the appropriate data for water from the Rusty Creek outflowing from the mine area, and for water from atmospheric precipitation. Isotope compositions of atmospheric precipitation water were taken from the reports of the station of Wola Justowska (city of Cracow), published by IAEA in Environmental Isotope Data No. 6-10 (1979-1994).

The dependence of the isotope composition of atmospheric precipitation directly on temperature and indirectly on the elevation above sea level is widely known. The average monthly values, calculated on the basis of 154 measurements, display a seasonal regularity, typical of the climate in Poland. The data of the year 1991 show the same general trend, though the regularity is less distinct because of lower number of measurements and the weather fluctuations. Although the data-collecting station was located *c.* 300 km east of Wieściszowice and was situated on different altitudes a.s.l., the seasonal isotope variation was pertinent to the latter area as well.

Comparison of the isotope composition of water from the Rusty Creek and from atmospheric precipitation indicates distinctly, that this creek is supplied mainly by ground waters. The annual values of isotope composition of the creek water distinctly were not influenced by characteristic seasonal isotope variation of the precipitation water. Isotope composition of the creek water (av. $\delta^{18}O = 9.67‰$, av. $\delta D = 64.9‰$) is close to that one of the ground waters in the Sudetes (Ciężkowski & Kryza 1989, Staśko 1994).

The isotope compositions of crystallization water in sulfate minerals (*see* Text-fig. 16) show distinct differences, resulting probably from various, still indefinite coefficients of isotope fractionation during mineral crystallization. Moreover, this effect is probably overlapped by variation of the isotope composition of solutions, the minerals crystallized from. Since both these values are unknown, it is difficult to use the isotope composition of the crystallization water to exact determination of the crystallization sequence of the minerals. Apparently, the oxygen isotope data suggest, that gypsum is the earliest mineral, and crystallization of the following minerals occurred from solutions, distinctly condensed by evaporation (higher $\delta^{18}O$ values). However, such conclusion is not confirmed by the hydrogen isotope data. Probably this controversy may be explained by the supposition, that crystallization took place from different solutions, influenced by seasonal isotope variations of atmospheric precipitation. Hence, the oxygen and hydrogen isotope compositions cannot be compared one to another.

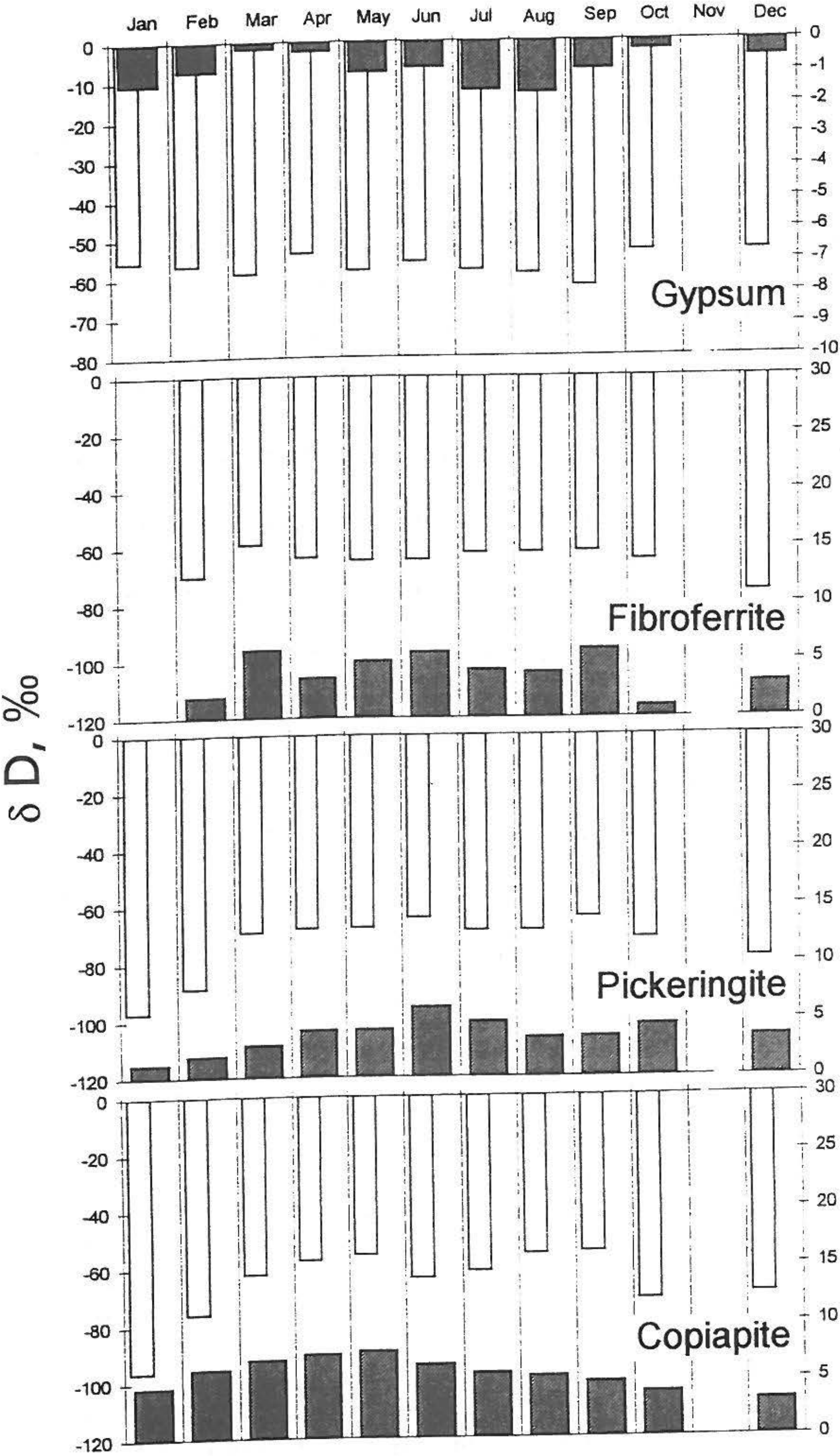


Fig. 16. Annual (during 1991) variation of oxygen and hydrogen isotopes in crystallization water of the sulfate minerals from Wieściszowice

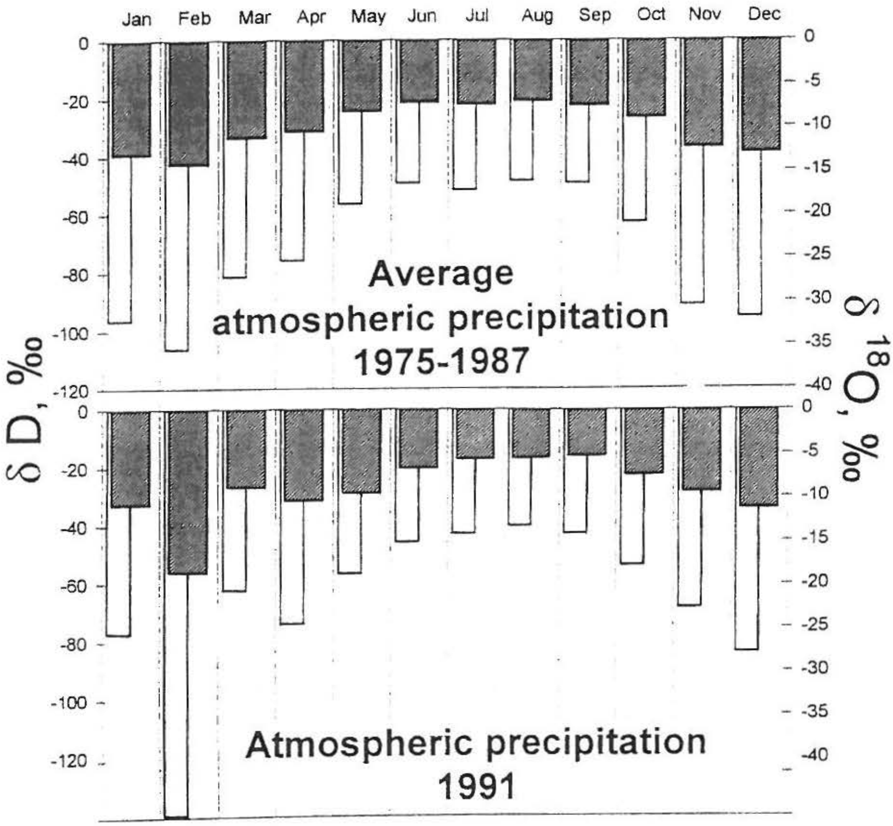


Fig. 17. Annual variation of oxygen and hydrogen isotopes in average atmospheric precipitation in 1975-1987, and in 1991

The analysis of the annual variation of the isotope composition of the crystallization water is more informative about the mineral origin conditions. The respective isotope data vary distinctly for individual minerals. Gypsum does not display annual isotope variations in its crystallization water. For fibroferrite the differences of the $\delta^{18}O$ and δD values for samples collected in winter and in summer are distinct, and even greater differences occur in copiapite and pickeringite. In all these cases the annual variation of the isotope composition of the crystallization water follows the annual changes in atmospheric precipitation (*compare* Text-figs 16 and 17), achieving maximum in summer, and minimum in winter. This indicates unambiguously, that the formation of the studied minerals is strongly influenced by atmospheric precipitation, to confirm quantitatively the general observations. The better soluble mineral, the more distinct is the influence of the seasonal changes of the atmospheric precipitation on the crystallization water.

The mechanism of the isotope exchange of the crystallization water is difficult to unambiguous recognition. It might have occurred due to repeated dissolution and crystallization from solutions of altering isotope composition, as it is suggested by correlation of the isotope changes with mineral solubility. Isotopic exchange of water in minerals without their dissolution is possible as well. In this case the differences between minerals may be explained by various binding energy of water molecules in the crystal lattices of the discussed minerals. Features of the above-reviewed structures of the sulfate minerals indicate, that crystallization water occupies various sites in the mineral structure: it may enter octahedrons coordinated with metal cations, or may be loosely bound by hydrogen bridges. The latter type of water molecules may be especially easy to exchange. Moreover, the hydrogen-bridge bonds may act with various intensity. In the gypsum structure, the water molecules occur in a dense network of the hydrogen bonds, thus their exchange is more difficult than exchange of a part of water in the structure of fibroferrite, copiapite or pickeringite, stabilized only by single hydrogen bridges. Seemingly, both the mechanisms of the isotope exchange play a certain part, but their importance may vary. In the case of poorly soluble minerals, as well as in the periods of lower humidity, the exchange in solid state is probable, whereas for well soluble minerals and humid periods the dissolution and recrystallization prevail. Because both the mechanisms result in the same effect of fitting of the isotope composition of crystallization water to the isotope composition of atmospheric precipitation, their distinguishing is of little importance.

MECHANISM OF PYRITE OXIDATION

Process of pyrite oxidation is in details a composed reaction, with its course difficult to an exact estimation. In general, two main modes of oxidation may be distinguished, where either molecular oxygen or ferric ion are the oxidizing agents, according to the reactions:

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad \textbf{(4)}$$

$$FeS_2 + 14\,Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad \textbf{(5)}$$

The development of the reaction (5) is controlled by the concentration of the ferric ion, which may be regenerated, according to the equation:

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2\,H_2O \quad \textbf{(6)}$$

Both modes of pyrite oxidation include a number of intermediate stages of a role not understood completely as yet. Elementary sulfur, sulfites, thiosulfates and polythionates may form as intermediate products (MOSES & HERMAN 1991). Experimental studies evidenced, that the amount of the intermediate products increases at higher pH (MOSES & *al.* 1987). For example, elementary sulfur may form only at pH >4.6. If oxidation occurs in strongly acid environment, concentrations of intermediate products are very low.

Oxidation of sulfides may also develop intensively due to activity of microorganisms, especially bacteria *Thiobacillus*. The acidophilic strain *Thiobacillus ferrooxidans*, common in acid mine waters, is especially active. Pyrite oxidation develops in some cases by direct bacterial activity on the pyrite crystal surface with use of the enzymatic transfer of electrons accompanying the oxidation of sulfur. The bacterial oxidation of Fe^{2+} to Fe^{3+} (reaction 6) is of great importance, because kinetics of inorganic oxidation of the bivalent to trivalent iron in acid solution is very low, limiting the role of ferric ions as the oxidizing agent. The vital activity of the bacteria *T. ferrooxidans*, obtaining energy for growth from oxidation of ferrous salts, may increase the kinetics even of six orders of magnitude. Both *T. ferrooxidans* and *T. thiooxidans* may obtain energy from enzymatic oxidation both sulfide- and intermediate-product-sulfur, *i.e.* that from sulfites and thiosulfates (TAYLOR & WHEELER 1994). Thus, bacteria may stimulate one or several of the stages of the pyrite oxidation of any of the two oxidation modes. It is probable, that in nature both inorganic and bacterial oxidation of pyrite are simultaneous and concurrent in certain stages.

Results of the works of TAYLOR & *al.* (1984) and VAN EVERDINGEN & KROUS (1985) suggested, that isotope analysis of oxygen in newly formed sulfate ion is a convenient mode to determine of the mechanisms of pyrite oxidation. In the reaction (4) as much as 87.5% oxygen included in sulfate ion come from molecular oxygen and the remaining 12.5% does from water. In the reaction (5) whole oxygen was taken from water, present in the reaction environment. If isotope compositions of atmospheric and water oxygen, and the respective oxygen isotope partition coefficients are known, it is possible to evaluate the quantitative fractions of the both reactions in formation of any sulfate by means of the following equation:

$$\delta^{18}O_{SO_4} = X(\delta^{18}O_{H_2O} + \varepsilon_{H_2O}) + (1 - X)[0.875(\delta^{18}O_{O_2} + \varepsilon_{O_2}) + 0.125(\delta^{18}O_{H_2O} + \varepsilon_{H_2O})] \quad (7)$$

where *X* means the fraction of oxygen derived from water, and ε – kinetic or equilibrium coefficients of isotope partition for the both oxygen sources. Atmospheric oxygen has the value of $\delta^{18}O$ equal 23.0‰ (KROOPNICK & CRAIG 1972) or 23.8‰, according to the data of HORIBE & *al.* (1973). The fractionation coefficient ε_{O_2} may achieve the value of –11.4‰ in the presence of the oxidizing bacteria, or -4.3‰ in the case of inorganic oxidation (TAYLOR & *al.* 1984). Isotope composition of oxygen of meteoric water, both ground- and precipitation one, in our geographic latitude is characterized by negative $\delta^{18}O$ and wide ranges of variation, as discussed earlier. The values of ε_{H_2O} are nil to +3.5‰, as determined by TAYLOR & *al.* (1984) for various oxidation conditions.

Thus, the isotope composition of oxygen in sulfates would depend mainly on composition of water of the reaction environment, as shown by the isoline, representing percentage of water oxygen in sulfates (Text-fig. 18). This method is especially useful at moderate and high latitudes, where meteoric waters are isotopically light. However, the results of the experimental works, collected by VAN STEMPVOORT & KRAUSE (1994) and TAYLOR & WHEELER (1994), evidenced that such model is too simplified and sometimes is not in agreement with nature. Major part of the determined oxygen isotope compositions of the sulfates, which formed due to sulfide oxidation in acid environment, is located in the field limited by the line of 100% water oxygen and that of the equation: $\delta^{18}O_{SO_4} = 0.62\delta^{18}O_{H_2O} + 9$. This means, that the sulfates formed by oxidation of pyrite either by inorganic mode or by bacterial activity bear mainly oxygen derived from water of the reaction environment. Sulfates, formed by natural oxidation of pyrite, contain essentially water oxygen as well (ŠMEJKAL 1979, TAYLOR & WHEELER 1994). Apparently the oxygen isotope studies cannot solve without doubts, which mechanism of pyrite oxidation occurred in an individual weathering zone. The process of the isotope exchange is probably the cause

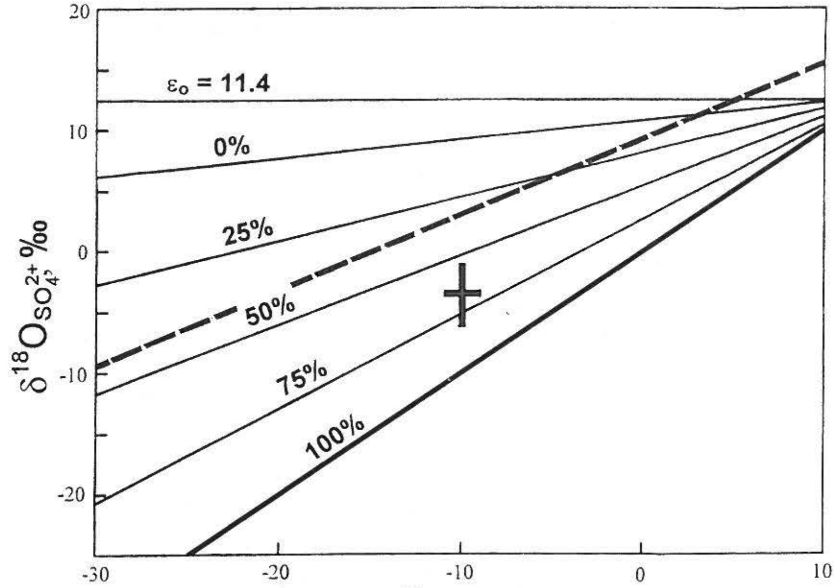


Fig. 18. Dependence of the oxygen isotope composition of the sulfates on the composition of water in the reaction environment

Heavy line indicates 100% oxygen derived from water; dashed line illustrates the experimentally chosen regression equation $\delta^{18}O_{SO_4} = 0.62\delta^{18}O_{H_2O} + 9$; cross points to the data obtained for the Wieściszowice samples of the isotope calibration of sulfates with respect to water in the case of oxidation by molecular oxygen. Such exchange occurs easily between the sulfite ion and acid water (van Stempvoort & Krause 1994). Hence, if sulfite is an intermediate product of pyrite oxidation, its oxygen isotope composition is fully controlled by isotope composition of water of the reaction environment. If sulfite ion is present in solution for a short time, the isotope exchange may be only partial. Other mechanisms of calibration of the isotope composition of oxygen in sulfate with respect to water, *e.g.* the immediate isotope exchange sulfate water, may be of certain importance only in strongly acid environment of $pH < 0$ (Taylor & Wheeler 1994).

On the basis of the performed oxygen isotope studies, an attempt was made to determine the source of oxygen in sulfates of the weathering zone at Wieściszowice. Though the direct measurements of the isotope composition of water from the pyrite oxidation environment were not made, without any significant mistake one may consider, that this composition was between those of groundwater and atmospheric precipitation of the area under study. The $\delta^{18}O$ measured values of water from the Rusty Creek and ranging from -9.5‰ in summer to -9.8‰ characterize the isotope composition of the shallow groundwater of the debris level well enough. The precipitation isotope composition may be determined by the mean annual $\delta^{18}O$ value of atmospheric water in Cracow equal -10.1, with the differences between the periods of summer (-8.0‰) and winter (-12.1‰). Without necessity to decide unambiguously, whether pyrite oxidation occurred in the environment of groundwater or directly in precipitation water, the acceptation of the value of *c.* -10‰ is seemingly reasonable for the environment of pyrite oxidation at Wieściszowice. Accepting the values of $\delta^{18}O = 23.8‰$, $\varepsilon_{O_2} = -11.4‰$ and $\varepsilon_{H_2O} = 0‰$, the equation (7) yields the water oxygen fraction in sulfates from 55 to 81%. The obtained values confirm, that a major part of sulfate oxygen during pyrite oxidation comes from water, not from molecular atmospheric oxygen, though they do not solve unambiguously the oxidation mechanism. All the collected data indicate, that in the weathering zone at Wieściszowice pyrite was mainly oxidized by ferric ion, despite the process development at the Earth's surface in the direct contact with atmospheric oxygen. This opinion is supported by characteristic high activity of Fe^{3+}, formed due to bacterial oxidation of ferrous salts. Bacteria *Thiobacillus ferrooxidans* are abundant in water of the Purple Pond, apparently they are common in humid parts of the mine workings. A typical occurrence of the Fe^{3+} minerals and almost complete absence of the Fe^{2+} minerals may be explained by the bacterial activity. Ivarson (1973) pointed to the special role of *T. ferrooxidans* in formation of the basic iron sulfates, especially jarosite, during pyrite oxidation. Common occurrence of these bacteria in acid mine waters and dump seepages, *i.e.* at the places where pyrite-bearing rocks are exposed to the weathering factors, evidences their important part in the process of the pyrite oxidation and formation of the weathering minerals, especially of the group of basic ferric sulfates.

CONDITIONS OF CRYSTALLIZATION AND STABILITY OF SULFATE MINERALS IN THE WEATHERING ZONE

An attempt was made to determine the crystallization conditions of the individual minerals, ranges of their stability and alteration modes on the basis of field observations and investigation results. At Wieściszowice any dependence of the crystallizing mineral species on the distance from the oxidized pyrite was not found. Pyrite relics of various preservation degrees occur in various sulfates. A distinct zoning of the discussed minerals was observed, apparently controlled by their solubility in water. The better solubility of a mineral, the more limited area of its occurrence, occupying dry parts of mine pits or dump, protected against humidity. Well-soluble minerals can crystallize only during rainless weather, being dissolved partly or completely in humid seasons. This way a selection of minerals develops in selected zones of the mine, causing formation of mono- or oligomineral accumulations at places of appropriate humidity.

Gypsum, the least soluble mineral of the paragenesis, may be found in the whole weathering zone, however, its monomineral radial aggregates of tabular crystals occur only at permanently wet places, *e.g.* at the adit mouth, where water seeps continuously. Other sulfates either could not crystallize, or would be dissolved and be washed away.

Fibroferrite, better soluble than gypsum, covers with almost monomineral crusts of several square meters the western walls of the open pit; it was found as well at other places that were quickly drying after rains. The total surface occupied by gypsum and fibroferrite does not decrease in winter, and both these minerals are clearly stable the whole year.

Copiapite and pickeringite are the minerals, whose occurrence is limited to the dry, insolated parts of the walls, especially of the southern exposure. These two minerals usually occur jointly: pickeringite needles grow commonly on the reniform aggregates of copiapite. Monomineral accumulations of these minerals were found exceptionally. Wet copiapite aggregates, which macroscopically seem to be pickeringite-free, on drying in room conditions cover with whitish, mold-like thin layer of pickeringite, crystallizing from remnant rock moisture. These two minerals are sensitive to atmospheric conditions. During humid seasons of the year their occurrence is limited to the places protected against water.

Slavikite in the estimated stability sequence should be located between fibroferrite and copiapite, closer to the first one. Slavikite aggregates are stable the whole year without legible traces of periodic crystallization.

Epsomite and alunogen are the least stable minerals of the studied paragenesis. They were found only occasionally at the driest places of the mine pits of dump after prolonged periods of rainless weather. Rainfalls dissolve these minerals, thus epsomite and copiapite are absent in autumn and winter.

The outlined scheme of the crystallization sequence in the sulfate paragenesis based on the mineral solubility in water, presents only an approximate mechanism of formation. In nature, the studied minerals crystallize not only by sequential precipitation from gradually concentrating solutions, but they are products of transformation of the older minerals as well. These transformations took place as partial or complete dissolution of certain minerals and formation of solutions, of high concentrations and special chemical compositions, from which younger minerals crystallized. This phenomenon is comparable, to some extent, to transformations of well-soluble evaporate minerals of the potassium-magnesium salt facies, though mineral parageneses are different. The transformation processes may develop by various modes, depending on the dissolving mineral species. Chemical composition of the new-formed local solutions determine the crystallizing minerals. Products of such transformations may be observed at the walls of the weathering schist rocks, and even better in the debris at the foot of the walls, where products of weathering accumulated and semiliquid masses of sulfate dripped. One observed there the alteration fibroferrite to slavikite and afterwards to pickeringite. Apparently, formation of alunogen and a part of epsomite was due to processes of transformation as well, namely those connected with separation of magnesium and aluminum from iron, when the latter was bound in less soluble minerals. Copiapite is the sole mineral, which was not transformed (only dissolved), what confirmed, that it is the most stable Fe III mineral of the discussed paragenesis. On drying in room conditions, small amounts of epsomite and alunogen crystallized relatively frequently in the sulfate samples from the moisture present in them, in addition to common pickeringite.

Observations of pyrite weathering under laboratory conditions and studies of the mineral parageneses of the pyrite weathering zones, developed in various climates allowed to establish a typical sulfate mineral succession, that developed at various distances from the parent sulfide. An ideal succession starts from the sulfates of iron II, which are closest to pyrite (szomolnokite, rhomboclase, rozenite, and melanterite). These minerals alter to sulfate of Fe II and Fe III (roemerite) and further to sulfates of Fe III (copiapite, fibroferrite, butlerite, coquimbite, hohmannite, botryogen, jarosite, and others). At the deposits of Chuquicamata, Quetena and Alcaparrosa in northern Chile of the classic, very well developed weathering zone, one found that according to the increasing distance from sulfides, acid salts altered to neutral and further to basic ones (BANDY 1938). The degree of hydration of the minerals increased in the same direction. Weathering zones of pyrite, formed in more humid climate were not devel-

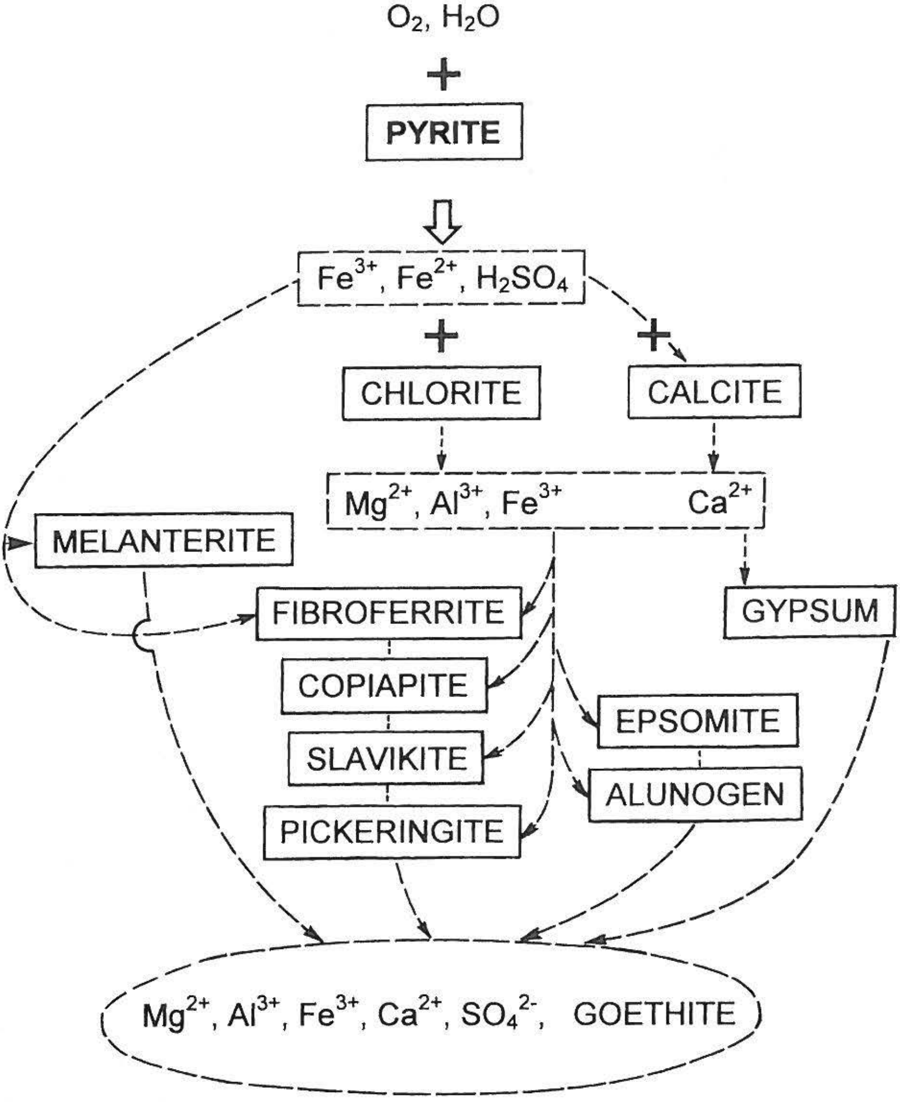


Fig. 19. Schematic diagram, to show the origin and evolution of the sulfate minerals in the weathering zone at Wieściszowice

oped so perfectly. In the temperate zone at most of the deposits, only certain minerals crystallize, whose appearance characterize local geochemical and hydrogeologic conditions. Nevertheless, sulfates bearing Fe^{2+} and Fe^{3+} are commonly present. Weathering of pyrite specimens, saved in room conditions, first produced ferrous sulfates, especially rozenite and halotrichite, afterwards ferrous-ferric sulfates, commonly roemerite, and finally ferric sulfates, most frequently copiapite (WIESE & *al.* 1987). At Wieściszowice similar regularities were not observed. Ferrous sulfates, except for rare melanterite, were not found. In the direct neighborhood of pyrite there occurred basic ferric sulfates, a prevailing mineral species group in the studied location. An absence of jarosite group minerals, which usually are common in similar associations, is a specific feature of the described weathering zone.

The genesis of the sulfate mineral assemblage found at Wieściszowice, according to the present-day stage of the studies, is summarized in a graph (Text-fig. 19).

CONCLUSIONS

The weathering zone, formed in the pyrite-bearing schists cropped out at the abandoned pyrite mine at Wieściszowice and submitted to intensive chemical superficial alteration, bears features the temperate climatic conditions, as in the Sudetes, infuenced by local geochemical pecliarities.

Both the modes and intensities of the weathering processes at Wieściszowice are characterized by the chemical composition of the surface- and shallow groundwaters of this mine region. The chemical composition is exemplified by water of the Purple Pond, occupying the mine pit bottom and collecting all products of the weathering. Water of this pond is strongly acidified with sulfuric acid (pH 2.6–2.8), mineralized (TDS 3–5.5 g per dm^3) and it contains 380–600 mg iron, 200–300 mg calcium, 150–250 mg magnesium and 90–170 mg aluminum per dm^3, and higher concentrations of many heavy metals.

Calculations of phase equilibria, performed with the use of hydrochemical data, show that chlorite was the least stable mineral of the schists and its decomposition supplied the solutions with appreciable amounts of magnesium, aluminum, and iron. Results of experimental decomposition of the schists in sulfuric acid solutions confirm the run of this natural process.

A rich sulfate mineral paragenesis found in the weathering zone at Wieściszowice consists of copiapite, pickeringite, fibroferrite, slavikite, gypsum, epsomite, melanterite, and alunogen. The performed studies yielded the correct chemical formula for slavikite as $MgFe_3[(OH)_3(SO_4)_4]\cdot 18H_2O$

and completed the characteristics of this still poorly known mineral. A similar mineralogical description was made for fibroferrite. In addition to the earlier known magnesiocopiapite, recognized is the occurrence of the varieties approaching the composition of aluminocopiapite. In the studied weathering zone there occurs pickeringite but not halotrichite. Unknown till present varieties of ferric pickeringite of appreciable substitution of Al by Fe^{3+} complete the list of the recognized species.

Isotope composition of sulfur in pyrite ($\delta^{34}S$ from 1.0 to 2.2‰) indicates a hydrothermal origin of the deposit and hypogene source of sulfur. The found small differentiation of isotope composition of sulfur in sulfate minerals resulted from their crystallization from solutions. Analyses of the oxygen isotope composition in sulfates show, that most of oxygen bound in sulfate ion is derived from water of the environment of the pyrite oxidation. The oxidation of pyrite by ferric ions, whose high concentration was caused by vital activity of the bacteria *Thiobacillus ferrooxidans*, was the most probable mechanism, which would explain almost complete absence of ferrous sulfates in the studied weathering zone and abundance of basic ferric sulfates. Isotope compositions of oxygen and hydrogen of crystallization water may be the indices of the crystallization conditions and stability of the sulfate minerals in the studied paragenesis. It was also stated that the better soluble mineral, the more distinct is the record of the seasonal changes of the isotope composition of the atmospheric precipitation water in the mineral crystallization water. Consequently, it is thought that all the processes recognized at Wieściszowice make up a developmental model of the weathering zone of the pyrite deposits, occurring in the silicate rocks, under temperate climatic conditions.

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REFERENCES

ATENCIO, D. & CARVALHO, F.M.S. 1994. Cell parameters for Mg-, Al- and Ni- synthetic end-members of the copiapite group. *Abstracts,* p. 21. *IMA 16th General Meeting, Pisa, Italy.*

AUGUST, C. 1984. Copiapite from Borów near Strzegom (Lower Silesia). *Miner. Pol.*, **15** (1/2), 79-90. Kraków.

BALL, J.W., NORDSTROM, D.K. & ZACHMANN, D.W. 1987. WATEQ4F a personal computer Fortran translation of the geochemical model WATEQ2 with revised data base. *USGS Open File Report*, pp. 87-50. Denver, Colorado.

BALCERZAK, E., DOBRZYŃSKI, D. & PARAFINIUK, J. 1992. The effects of mineral alterations on the chemical composition of waters in the weathered zone of pyrite-bearing schists in Wieściszowice, Rudawy Janowickie Mts, W Sudetes, Poland. [In Polish]. *Ann. Soc. Géol. Polon.*, **62** (1), 75-93. Kraków.

BANDY, M.C. 1938. Mineralogy of three sulphate deposits of northern Chile. *Amer. Miner.*, **23** (11), 669-760. Menasha, Wisconsin.

BAYLISS, P. & ATENCIO, D. 1985. X-ray powder diffraction data and cell parameters for copiapite-group minerals. *Canad. Miner.*, **23**, 53-56. Ottawa.

BERRY, L.G. 1947. Composition and optics of copiapite. *Univ. Toronto Stud., Geol.*, **21**, 21-34. Toronto.

CATHLES, L.M. 1994. Attempts to model the industrial-scale leaching of copper-bearing mine waste. *In*: C.N. ALPERS & D.W. BLOWES (*Eds*), Environmetal Geochemistry of Sulfide Oxidation. *ACS Symposium Series*, **550**, 123-131. Washington, D.C.

CÉSBRON, F. 1964. Contribution a la minéralogie des sulfates de fer hydrates. *Bull. Soc. Franc. Miner. Crist.*, **87**, 125-143. Paris.

CIĘŻKOWSKI, W. & KRYZA, J. 1989. Deuterium and oxygen-18 in fresh groundwater in Sudetes. [In Polish]. *Prace Naukowe Instytutu Geotechniki Pol. Wrocł.*, **58** (29). Wrocław.

COLEMAN, M.L., SHEPHERD, T.J., DURHAM, J.J., ROUSE, J.E. & MOORE, G.R.1982. Reduction of water with zinc for hydrogen isotope analysis. *Anal. Chem.*, **54**, 993-995. Washington, D.C.

DOBRZYŃSKI, D. 1995. Aluminium solubility in acid waters of the abandoned open pyrite mine at Wieściszowice (Rudawy Janowickie Mts., West Sudetes). *Geol. Quart.*, **39** (2), 241-254. Warszawa.

DZIEKOŃSKI, T. 1972. Wydobywanie i metalurgia kruszców na Dolnym Śl1sku od XIII do połowy XX wieku. *Ossolineum*; Wrocław.

ENVIRONMENTAL ISOTOPE DATA No. 6. 1979. World Survey of Isotope Cncentration in Precipitation (1972-1975). *Technical Reports Series IAEA*, **192**. Vienna.

ENVIRONMENTAL ISOTOPE DATA No. 7. 1980. World Survey of Isotope Concentration in Precipitation (1976-1979). *Technical Reports Series IAEA*, **226**. Vienna.

ENVIRONMENTAL ISOTOPE DATA No. 8. 1986. World Survey of Isotope Concentration in Precipitation (1980-1983). *Technical Reports Series IAEA*, **264**. Vienna.

ENVIRONMENTAL ISOTOPE DATA No. 9. 1990. World Survey of Isotope Concentration in Precipitation (1984-1987). *Technical Reports Series IAEA*, **311**. Vienna.

ENVIRONMENTAL ISOTOPE DATA No. 10. 1994. World Survey of Isotope Concentration in Precipitation (1988-1991). *Technical Reports Series IAEA*, **371.** Vienna.

EPSTEIN, S. & MAYEDA, T. 1953. Variation of ^{18}O content of waters from natural sources. *Geochim. Cosmochim. Acta*, **4**, 213-224. Oxford.

FANFANI, L., NUNZI, A., ZANAZZI, P.F. & ZANZARI, A.R. 1973. The copiapite problem: the crystal structure of a ferrian copiapite. *Amer. Miner.*, **58**, 314-322. Lawrence, Kansas.

FLEISCHER, M. 1983. Glossary of Mineral Species. *Mineralogical Record*; Tucson, Arizona.

FRITZ, P., BASHARMAL, G.M., DRIMMIE, R.J., IBSEN, J. & QURESHI, R.M. 1989. Oxygen isotope exchange between sulphate and water during bacterial reduction of sulphate. *Chem. Geol.*, **79**, 99-105. Amsterdam.

FRY, B., RUF, W., GEST, H. & HAYES, J.M. 1988. Sulfur isotope effects associated with oxidation of sulfide by O_2 in aqueous solution. *Chem. Geol.*, **73**, 205-210. Amsterdam.

GARAVELLI, C. 1955. Ricerche su alcuni solfati del giacimento ferrifero di Terranera (Isola Elba). *Rend. Soc. Ital. Min. Petr.*, **11**, 100-146. Roma.

GRINENKO, V.A. & GRINENKO, L.N. 1974. Sulphur Isotope Geochemistry. [In Russian]. *Nauka*; Moskva.

HAŁAS, S. & WOŁĄCEWICZ, W. 1981. Direct extraction of sulfur dioxide from sulfates for isotopic analysis. *Anal. Chem.*, **53**, 685-689. Washington, D.C.

HORIBE, Y., SHIGEHARA, K. & TAKAKUWA, Y. 1973. Isotope separation factor of carbon-dioxide-water system and isotopic coposition of atmospheric oxygen. *J. Geophys. Res.*, **78**, 2625-2629. Washington, D.C.

HRYNIEWICZ, R. & PRZYBYLSKA, G. 1993. Zanieczyszczenie opadów atmosferycznych w Polsce. *In*: I. DYNOWSKA (*Ed.*), Przemiany stosunków wodnych w Polsce w wyniku procesów naturalnych i antropogenicznych; pp. 11-52. Kraków.

IVANOVA, V.P., KASATOV, B.K., KRASAVINA, T.N. & ROZINOVA, E.L. 1974. Thermal analysis of minerals and rocks. [In Russian]. *Niedra*; Leningrad.

IVARSON, K.C. 1973. Microbiological formation of basic ferric sulfates. *Canad. J. Soil Sci.*, **53**, 315-323. Ottawa.

JAMBOR, J.L. & TRAILL, R.J. 1963. On rozenite and siderotil. *Canad. Miner.*, **22**, 751-763. Ottawa.

JANECZEK, J., KOZŁOWSKI, K. & ŻABA, J. 1991. Zbieramy minerały i skały. Przewodnik po Dolnym Śląsku. *Wyd. Geol*; Warszawa.

JASKÓLSKI, S. 1961. Versuch einer Klärung des Entstehens der in Wieściszowice (Niederschlesien) vorkommenden pyritischen Schiefer. *Bull. Acad. Polon. Sci., Sér. Sci. Chim. Géol. Géogr.*, **9** (4). Warszawa.

— 1964. On the origin of pyrite schists at Wieściszowice (Lower Silesia). [In Polish]. *Ann. Soc. Gol. Polon.*, **34** (1/2), 29-64. Kraków.

JIANG, W.T., PEACOR, D.R. & BUSECK, P.R. 1994. Chlorite geothermometry? Contamination and apparent octahedral vacancies. *Clays & Clay Miner.*, **42** (5), 593-605. Lawrence, Kansas.

JIRKOVSKÝ, R. & ULRICH, F. 1926. Slavíkit, novy mineral. *Vest. Stat. Geol. Ust. Česk. Rep.*, **2**, 348-351. Praha.

JOLLY, J.H. & FOSTER, H.L. 1967. X-ray diffraction data of aluminocopiapite. *Amer. Miner.*, **52**, 1221-1223. Menasha, Wisconsin.

KOWALSKI, W. 1977. Geochemistry, mineralogy and origin of the Lower Silesian barite deposits and occurences, Part II. [In Polish]. *Arch. Miner.*, **33** (1), 107-167. Warszawa.

KROOPNICK, P. & CRAIG, H. 1972. Atmospheric oxygen: isotopic composition and solubility fractionation. *Science*, **175**, 54-55. Washington, D.C.

KROUSE, H.R. 1980. Sulphur isotopes in our environment. *In*: P. FRITZ & J.C. FONTES (*Eds*), Handbook of Environmental Isotope Geochemistry. **1**. The Terrestrial Environment, 435-471. *Elsevier*; Amsterdam.

KUBISZ, J. 1964. Studies on supergene sulphate minerals occurring in Poland. [In Polish]. *Prace Geol. Kom. Nauk Geol. PAN*, **26**, 1-76. Warszawa.

KOURIMSKÝ, J., 1971. Über Fibroferrit von Zličin bei Prag. [In Czech]. *Acta Musei Nat. Pragae*, **27 B** (1), 1-10. Praha.

LOVAS, G.A. 1986. Structural study of halotrichite from Recsk (Matra Mts., N-Hungary). *Acta Geol. Hungar.*, **29** (3/4), 389-398. Budapest.

MAKOVICKÝ, E. & STREŠKO, V. 1968. Slavikite from Medzev near Košice, Czechoslovakia. *Tscherm. Miner. Petr. Mitt.*, **12** (1), 100-107. Wien.

MAZUR, L. 1962. X-ray chemical investigation of the sulphate products of pyrite decay appearing in Dobrzyń on the Vistula. [In Polish]. *Stud. Soc. Sci. Torunensis*, **4** (2), 1-17. Toruń.

MENCHETTI, S. & SABELLI, C. 1976. The halotrichite group: the crystal structure of apjohnite. *Miner. Mag.*, **40**, 599-608. London.

MICHNIEWICZ, M. 1981. Some results of hydrochemical studies on eastern cover of the Karkonosze granite. [In Polish]. *Kwart. Geol.*, **25**, 185-198. Warszawa.

MIZUTANI, Y. 1971. An improvement in the carbon-reduction method for the oxygen isotopic analysis of sulphates. *Geochem. J.*, **5** (2), 69-77. Tokyo.

MOSES, C.O., NORDSTROM, D.K., HERMAN, S. & MILLS, A.L. 1987. Aqueous pyrite oxidation by dissolved oxygen and by ferric iron. *Geochim. Cosmochim. Acta*, **51** (6), 1561-1571. Oxford.

Moses, C.O. & Herman, J.S. 1991. Pyrite oxidation at circumneutral pH. *Geochim. Cosmochim. Acta*, **55** (2), 471-482. Oxford.

Nielsen, H. 1985. Sulfur isotope ratios in strata-bound mineralizations in Central Europe. *Geol. Jb.*, **D 70**, 225-262. Hannover.

Nielsen, H. & Ricke, W. 1964. Schwefel-Isotopenverhaeltnisse von Evaporiten aus Deutschland; Ein Beitrag zur Kenntnis von $d^{34}S$ im Meerwasser-Sulfat. *Geochim. Cosmochim. Acta*, **28**, 577-591. Oxford.

Nielubowicz, R. & Jaskólski, S. 1957. Materials to the knowledge of pyrite shales deposits in Wieściszowice (Lower Silesia) and their origin. [In Polish]. *Przegl. Geol.*, **7**, 303-310. Warszawa.

Nissenbaum, A. & Rafter, T.A. 1967. Sulfur isotopes in altered pyrite concretions from Israel. *J. Sedim. Petr.*, **37** (3), 961-962. Menasha, Wisconsin.

Ohmoto, H. & Rye, R.O. 1979. Isotopes of carbon and sulfur. *In*: H.L. Barnes (*Ed.*), Geochemistry of Hydrotermal Ore Deposits, pp. 509-567. *Holt, Rinehart & Winston*; New York.

Pačes, T. 1985. Sources of acidification in Central Europe estimated from elemental budgets in small basins. *Nature*, **315**, 31-36. London.

Palache, C., Berman, H. & Frondel, C. 1951. Dana's system of mineralogy, **2**, pp. 620-621, *John Wiley & Sons;* New York.

Parafiniuk, J. 1991. Fibroferrite, slavikite and pickeringite from the oxidation zone of pyrite-bearing schists in Wieściszowice (Lower Silesia). *Miner. Pol.*, **22** (1), 3-15. Kraków.

— 1994. Sulphate weathering minerals from the mica schist quarry in Krobica (West Sudeten, SW Poland). [In Polish]. *Przegl. Geol.*, **7**, 536-538. Warszawa.

— & Dobrzyński, D. 1995. Geochemical processes forming the chemical composition of water in the area of abandoned pyrite mine at Wieściszowice (Lower Silesia, SW Poland). [In Polish]. *Współczesne Problemy Hydrogeologii*, **7**, 375-382. Kraków – Krynica.

Piestrzyński, A. & Salamon, W. 1977. New data on polymetallic mineralization of quartz veins in pyrite deposit from Wieściszowice (Lower Silesia). [In Polish]. *Kwart. Geol.*, **21**, 27-35. Warszawa.

Perroud, P., Meisser, N. & Sarp, H. 1987. Presence de zincopiapite en Valais. *Schweiz. Miner. Petr. Mitt.*, **67** (1/2), 115-117. Zürich.

Petrascheck, W.E. 1933. Die Erzlagerstätten des schlesischen Gebirges. *Archiv f. Lagerstättenforschung*, **59**, Berlin.

Plummer, L.N., Jones, B.F. & Truesdell, A.J. 1976. WATEQF - Fortran IV version of WATEQ, a computer program for calculating chemical equilibrium of natural waters. *USGS, Water Resour. Invest., WRI,* **76-13**, pp. 1-61. Denver, Colorado.

Raab, M. & Spiro, B. 1991. Sulfur isotopic variation during seawater evaporation with fractional crystallization. *Chem. Geol.* **86**, 323-333. Amsterdam.

Sabelli, C. & Santucci, A. 1987. Rare sulfate minerals from the Cetine mine, Tuscany, Italy. *N. Jb. Miner. Mh.*, **4**, 171-182. Stuttgart.

Scordari, F. 1981. Fibroferrite: a mineral with a $\{Fe(OH)(H_2O)_2SO_4\}$ spiral chain and its relationship to $Fe(OH)SO_4$, butlerite and parabutlerite. *Tscherm. Miner. Petr. Mitt.*, **28** (1), 17-29. Wien.

Šmejkal, V. 1979. Oxygen isotopic composition of sulphates from some mineral waters and mine waters in western Bohemia. *Isotope Hydrology 1978*, IAEA, **1**, 83-98. Wien.

Smirnov, S.S. 1956. Strefa utlenienia złóż siarczkowych, pp. 1-317. *Wyd. Geol.*; Warszawa.

Smulikowski, W. 1995. Skały stilpnomelanowe we wschodniej okrywie granitu Karkonoszy. *PTMin. Prace Specj.*, **6**, 83-85. Kraków.

Staśko, S. 1994. Groundwater age and source areas in Polish Sudetes base on ^3H, ^2H and ^{18}O isotopes data. *Isotope Workshop II, Ext. Abstr. International Isotope Society and University of Wrocław*, pp. 140-141. Wrocław.

Stępisiewicz, M. 1983. Sideronatrite and copiapite from Turoszów, Lower Silesia. *Arch. Miner.*, **38** (2), 35-44. Warszawa.

Sullivan, P.J., Mattigod, S.V. & Sobek, A.A. 1986. Dissolution of iron sulfates from pyritic coal waste. *Environ. Sci. Technol.*, **20**, 1013-1016. Easton – Pasadena.

Süsse, P. 1972. Crystal structure and hydrogen bonding of copiapite. *Zeitschr. Krist.*, **135**, 34-55. Frankfurt a.M.

— 1975. Struktur und Kristallchemie des Slavikits, $NaMg_2Fe_5(SO_4)_7(OH)_6x33H_2O$. *N. Jb. Miner. Mh.*, 27-40. Stuttgart.

SVERDRUP, H.U. 1990. The kinetics of base cation release due to chemical weathering, pp. 1-246. *Lund University Press*; Lund.

SZCZEPAŃSKA, J. 1987. Coal mine spoil tips as a source of the natural water environment pollution. [In Polish]. *Zesz. Nauk. AGH, Geologia*, **35**, 1-122. Kraków.

TAYLOR, B.E. & WHEELER, M.C. 1984. Stable isotope geochemistry of acid mine drainage: Experimental oxidation of pyrite. *Geochim. Cosmochim. Acta*, **48**, 2669-2678. Oxford.

— 1994. Sulfur- and oxygen-isotope geochemistry of acid mine drainage in the Western United States: field and experimental studies revisited. *In*: C.N. ALPERS & D.W. BLOWES *(Eds)*, Environmental Geochemistry of Sulfide Oxidation. *ACS Symposium Series*, **550**, 481-514. Washington, D.C.

TEISSEYRE, J.H. 1971. On the age and sequence of beds in the metamorphic rocks of the Rudawy Janowickie range and Lasocki Ridge. [In Polish]. *Geol. Sudetica*, **5**, 165-210. Warszawa.

— 1973. Metamorphic rocks of the Rudawy Janowickie and Lasocki Grzbiet ranges. [In Polish]. *Geol. Sudetica*, **8**, 7-120. Warszawa.

THODE, H.G. & MONSTER, J. 1965. Sulfur isotope geochemistry of petroleum, evaporites, and ancient seas. *Amer. Assoc. Petr. Geol. Mem.*, **4,** 367-377. Tulsa, Oklahoma.

TOUSSAINT, J. 1955-56. Sur la fibroferrite et ses produits de déshydratation. *Ann. Soc. Géol. Belgique*, **79 B**, 45-52. Liège.

TREMBACZOWSKI, A. 1991. Sulphur and oxygen isotopes behaviour in sulphates of atmospheric groundwater system observations and model. *Nordic Hydr.*, **22**, 46-66. Lyngby.

TU KWANG-CHIH, LI HSILIN, HSIEH HSEN-DEH & YIN SHU-SEN, 1964. Zincbotryogen and zinc-copiapite two new varieties of sulphate minerals. *Acta Geol. Sinica*, **44** (1), 100-101. Beijing.

VAN EVERDINGEN, R.O. & KROUSE, H.R. 1985. Isotope composition of sulphates generated by bacterial and abiological oxidation. *Nature*, **315** (6018), 395-396. London.

VAN STEMPVOORT, D.R. & KROUSE, H.R. 1994. Control of $d^{18}O$ in sulfate. Review of experimental data and application to specific environments. *In*: C.N. ALPERS & D.W. BLOWES *(Eds)*, Environmetal Geochemistry of Sulfide Oxidation. *ACS Symposium Series*, **550**, 446-480. Washington, D.C.

VAN TASSEL, R. 1972. Slavikite – a review. *Acta Musei Nat. Pragae*, **28 B** (1/2), 1-14. Praha.

WIESE, R.G., POWELL, M.A. & FYFE, W.S. 1987. Spontaneous formation of hydrated iron sulfates on laboratory samples of pyrite- and marcasite-bearing coals. *Chem. Geol.*, **63**, 29-38. Amsterdam.

WIESER, T. 1949. Sulphate weathering products on the iron disulphide deposit of the Holy Cross Mts. [In Polish]. *Ann. Soc. Géol. Polon.*, **19** (3), 445-447. Kraków.

— 1978. Glaucophane schists and associated rocks of Kopina Mt. (Lasocki Range, Sudeten). *Miner. Pol.*, **9** (1), 17-40. Kraków.

WIEWIÓRA, A. & WEISS, Z. 1990. Crystallochemical classifications of phyllosilicates based on the unified system of projection of chemical composition: II. The chlorite group. *Clay Miner.*, **25**, 83-92. Cambridge.

WRZODAK, J. 1962. Studium mineralogiczno-gochemiczne strefy utleniania złoża łupków pirytonośnych w Wieściszowicach na Dolnym Śląsku. *Archiwum IGMiP Uniwersytetu Warszawskiego*.

WYSZOMIRSKI, P. 1992. Uranium-bearing copiapite from kaolin deposit in Żarów (Lower Silesia, Poland). *Miner. Pol.*, **23** (2), 43-52. Kraków.

ZAJIC, J.E. 1969. Microbial biogeochemistry, pp. 1-343. *Academic Press*; New York – London.

ZODROW, E.L.1980. Hydrated sulfates from Sydney Coalfield, Cape Breton Island, Nova Scotia, Canada: the copiapite group. *Amer. Miner.*, **65** (9/10), 961-967. Washington, D.C.

ŻABIŃSKI, W. 1960. The mineralogical characteristic of the oxidation zone of Silesia Cracow zinc and lead deposits. [In Polish]. *Prace Geol. Kom. Nauk Geol. PAN,* **1**, 1-99. Kraków.