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MINERAL CRUSTS OF THE SURFACE WEATHERING ZONE OF SANDSTONE TORS IN THE POLISH CARPATHIANS

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Abstract. Secondary mineral crusts are a common phenomenon occurring on the wall surfaces and the near-surface zones of sandstone tors in the Polish Flysch Carpathians. They form laminae up to a few mm in thickness of fill up irregularly the intergranular spaces. Laboratory investigation has shown that they generally consist of gypsum, gypsum and clay minerals, clay minerals, cristobalite, or cristobalite and clay minerals. Clay minerals are represented by illite, kaolinite and montmorillonite. The mineral aggregates are contaminated by detrital constituents, mainly by quartz grains. Epigenetic minerals owe their origin to the chemical weathering of rock-forming minerals, in which rainwater containing atmospheric sulphur compounds plays a significant role. The precipitation of secondary minerals results in the local loosening of the structure of sandstones and eventually in the exfoliation of tor walls.

INTRODUCTION

The original features of the relief of the Flysch Carpathians are tors made up of coarse-grained sandstones and conglomerates (Phot. 1). In contrast to other rock outcrops, they show greater durability and are subject to the action of atmospheric agents for a long time.

In the Polish Flysch Carpathians there occur three genetic types of tors, owing their origin to denudation, slumps and erosion (Alexandrowicz 1978 a, b). Of the three, denudation tors are most suitable for the studies of weathering processes in sandstones and conglomerates as being best modelled by the prolonged action of atmospheric agents. They occur in relatively resistant zones, in thick complexes of sandstones and conglomerates. During the denudation of ridge crests and the recession of slopes, the elements of resistance could have been preserved on the ground surface in the form of rock outcrops. The periods of intense denudation were particularly favourable to the formation of tors of the type discussed.

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The tors found at present in the Flysch Carpathians formed under the periglacial conditions of the Würm (Czudek, Demek, Stehlik 1965; Demek 1966, 1969; Baumgart-Kotarba 1974; Alexandrowicz 1978 a, b). The outcrops of sandstone beds denuded then on the slopes and ridge crests were initially, in the pleniglacial period (25,000—15,000 years BP), modelled mainly by intense physical weathering processes. As the climate became warmer and the humidity and insolation increased, chemical weathering began to play an increasingly important part in the shaping of tors, reaching the highest intensity in the Holocene, i.e. in the past 10,000 years.

The course of weathering under definite climatic conditions is variable, depending on the type of sandstone rocks, the kind, amount and distribution of their cement, and the composition and size of detrital grains. Moreover, the process is expedited by fractures and sedimentary discontinuities of various kinds, as these provide main channels of migration for rainwater and solutions cantaining dissolved mineral matter.

The denudation rocks occurring in the Flysch Carpathians are made up of sandstones and conglomerates of the type of fluxoturbidites, i.e. of untypical flysch sediments deposited by submarine sand flows (Dżułyński, Książkiewicz, Kuenen 1959). The characteristic features of tors are: the considerable thickness of beds (up to one or even a few m), the lack or sporadic presence of thin shale layers, the dominance of coarse sand and gravel fractions, the poor sorting of components, synsedimentary disturbances of beds, the uneven distribution of cement, mainly clayey or clay-ferruginous, or of the matrix type in ultracoarse-grained rocks, low volume weight and high absorption of water weight.

In the Polish Flysch Carpathians the occurrence of tors is confined to some lithostratigraphic members only, mainly of the Silesian and Magura nappes, which are widespread in this area. In the western part of the Silesian nappe, notable tor complexes are the Godula sandstones (conglomerates from Malinowska Skała), Istebna and Ciężkowice sandstones, and in the Eastern Carpathians — the Krosno sandstones. Within the Magura nappe, numerous tors occur within the outcrops of thick-bedded sandstones of the Magura Beds and older complexes, aspecially those belonging to the Inoceramian-Beloveza Beds, now referred to as the Ropianica Beds. Sporadically tors made up of the Ciężkowice sandtones of this series can be found. There are also few tors within the Dukla (Fore-Magura) nappe, mainly in the sandstone horizon from Mszanka in the Beskid Niski Mts. The sandstones and conglomerates of these beds differ in the nature of cement and the mineralogical composition, particularly in the content of feldspars, femic minerals and glauconite.

The general transformation mechanism of the microrelief of tors involves the migration of chemical substances dissolved in rainwater from the bedrock towards the surface of tors, the formation of new compounds and their precipitation. One of the manifestations of chemical weathering is secondary mineral aggregates precipitated in the form of crusts and efflorescences in the outermost zones of tors (Phot. 2). The crusts collected from the walls of tors of different types in the Polish Flysch Carpathians were subjected to detailed mineralogical investigations.

OCCURRENCE OF SECONDARY WEATHERING MINERALS

The mineral aggregates occurring in the weathering zones of tors assume diverse forms. In spite of their inconsiderable thickness, generally about 1 mm, they are conspicuous against grey sandstone or conglomerate. They are white, white-grey or pinkish coatings varying in hardness from compact crusts to ones crumbling to powder when touched. The hardest of these have a glassy lustre and a distinct crustal structure.

Secondary weathering minerals occur locally. They coat unevenly fragments of tor walls, irrespective of their exposition, and are often found only between the grains of sandstones and conglomerates. They are particularly common on well-modelled tors, on their surfaces subject to exfoliation. Sporadically they have been noted on rift tors and tors in the form of ruins, on their even joint faces.

The following modes of occurrence of secondary mineral crusts have been noted in the Polish Flysch Carpathians:

1 — hard crusts coloured yellow by iron oxides occurring on indurated surfaces at various stages of modelling, not subject to exfoliation or showing laminar exfoliation;

2 — crumbly aggregates, generally white in colour, on the surface of sandstone under the consolidated outer crust subject to exfoliation, and on rock fragments freshly exposed by exfoliation;

3 — crusts of various consistencies on the inside of small exfoliation flakes up to 2 mm in thickness resembling dried mud;

4 — white powder dispersed as a substance impregnating the cement of sandstones and conglomerates within exfoliation flakes or on the surfaces not subject to exfoliation;

5 — hard crusts on joint faces and ferruginous fissure coatings and under their exfoliation flakes.

Similar mineral crusts have been reported from the walls of tors made up of Upper Cretaceous sandstones in Czechoslovakia and from sandstone tors in the Roumanian Carpathians, especially in the Bucega range (Southern Carpathians).

The crusts collected from tors were sorted out according to the mode of their occurrence and the kind of sandstones and conglomerates, and 36 samples were selected for detailed studies. These were samples collected into glass vials directly from mineral crusts or, in ten cases, together with fragments of rocks on which they were found.

EXPERIMENTAL

The samples collected from the weathering zones of tors containing secondary mineral crusts were subjected to investigation using X-ray, microscopic and chemical methods. The aim of this investigation was to determine the composition and amount of secondary minerals associated genetically with chemical weathering, and to determine the degree of alteration of rock-forming minerals in the weathering zone of tors in order to explain the processes of formation of the secondary minerals.

X-ray diffraction patterns were recorded for all the selected samples (36) with a DRON-2.5 diffractometer, using Fe-filtered CuK_{α} radiation.

The instrument settings were: slits 0.6/1.2, sensitivity 1, compensation 0, chart speed 600 mm/hr. The patterns were interpreted using Micheev's (1957) key to minerals and the ASTM tables. Two samples of parent rock, collected from the outermost zones of tors containing secondary mineral cruusts, were subjected to electron microprobe analysis. A Cameca probe was used, and the samples were coated with gold. Thin sections of 10 sandstone samples with secondary mineral concentrations were examined under the polarizing microscope. Atomic absorption analysis was carried out on 5 samples to determine experimentally the rates at which elements from rocks go into solution. After drying and weighing, the samples were immersed in slightly acidified (1 ml H_2SO_4/200 ml H_2O) distilled water and kept in beakers for 4 days without stirring, whereupon the extracts were transferred with a pipette into flasks and analysed for Ca, Mg, Na, K, Mn and Fe. H_2SO_4 was used to acidify water as an acid occurring under natural conditions, the presence of which in rainand groundwater is the primary agent altering carbonates to sulphates.

RESULTS

The weathering crusts occurring in the outermost zones of tors are mineral aggregates of varying composition. Their dominant constituent is detrital quartz, generally accompanied by plagioclases and calcite present in varying proportions. Potassium feldspars and micas are scarce. All these components owe their oring to the disintegration of sandstone and form an admixture in the secondary mineral aggregates produced by chemical weathering and consisting of gypsum, illite, kaolinite, montmorillonite and cristobalite (Figs. 1—4). There are five different combinations of coexistance of these minerals: gypsum, gypsum and clay minerals, clay minerals, cristobalite, cristobalite and clay minerals (Table 1). Most samples consist entirely of gypsum or of gypsum accompanied by clay minerals in the following associations: gypsum-illite, gypsum-kaolinite, gypsum-montmorillonite, gypsum-illite-montmorillonite, gypsum-illite-kaolinite-montmorillonite. The content of gypsum varies from trace amounts

Table 1

The occurrence of epigenetic minerals in the surface zones of sandstone tors in the Polish Carpathians

Series	Lithostratigraphic member	Gypsum	Gypsum, clay minerals	Clay minerals	Cristobalite	Cristobalite, clay minerals
Magura	Magura sandstones	+	+	+	+	+
Dukla	Mszanka sandstones	+	+			
	Krosno sandstones		+			
Silesian	Ciężkowice sandstones	+	+			
	Istebna sandstones	+	+	+		

up to 40 %, while that of the ceoxisting clay minerals is generally not more than a few per cent. The presence of gypsum or gypsum accompanied by clay minerals is typical of tors made up of sandstones of all types (Table 1). Clay minerals which are the sole constituent of some crusts are represented by illite, illite and kaolinite, or illite and montmorillonite. Their few occurrences have been reported from the Magura and Istebna sandstones. Cristobalite occurring alone or with a small admixture of

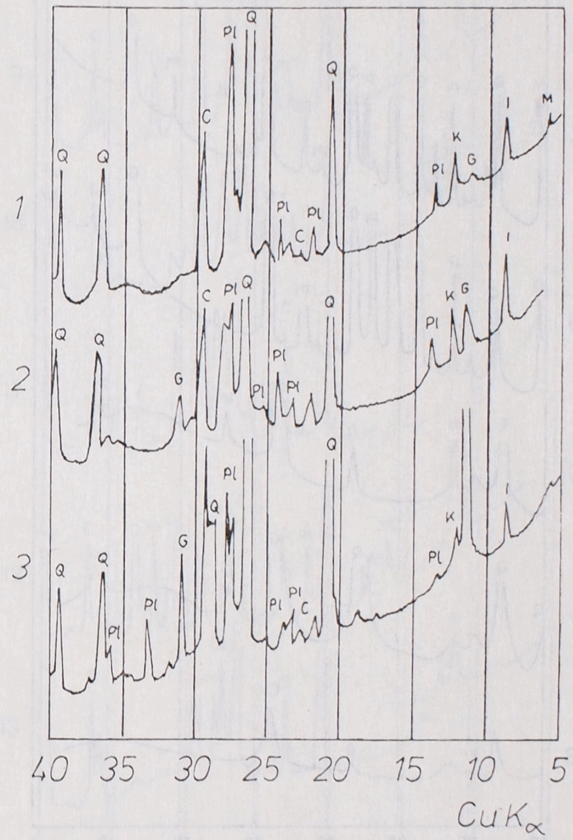


Fig. 1. X-ray diffraction patterns of weathering mineral aggregates of sandstone tors
G — gypsum, I — illite, K — kaolinite, M — montmorillonite, Cr — cristobalite, Q — quartz, Pl — plagioclases, Sk — potassium feldspars, C — calcite. *1* — Żywiec Beskid Mts — Czarny Groń, Magura sandstones, *2* — Żywiec Beskid Mts — Weska, Magura sandstones, *3* — Beskid Wyspowy Mts — Luboń Wielki, Magura sandstones (nature reserve)

montmorillonite forms hard scales on the walls of tors covered by sandstone crusts with a ferruginous cement. Cristobalite has been found in three samples collected from the walls of tors occurring within the outcrops of the bottom beds of the Magura sandstone near Mrukowa in the Beskid Niski Mountains, where its content is dominant.

At the present stage of investigation, a comparison of the occurrence of epigenetic minerals in the respective lithostratigraphic members has shown that mineral crusts derived from the Magura sandstones exhibit greatest mineralogical diversity (Table 1).

The examination of thin sections has revealed that the sediments making up tors have a psammitic or psephitic-psammitic texture and random structure. Dominant are angular or poorly rounded grains. Sometimes metasandstone grains with a siliceous cement are visible (Phot. 3). Irregular concentrations of quartz grains form the matrix. In all thin sections feldspars and micas have been observed. The former are both plagioclases and potassium varieties, generally represented by orthoclase sometimes accompanied by smal amounts of microcline and scarce, perthi-

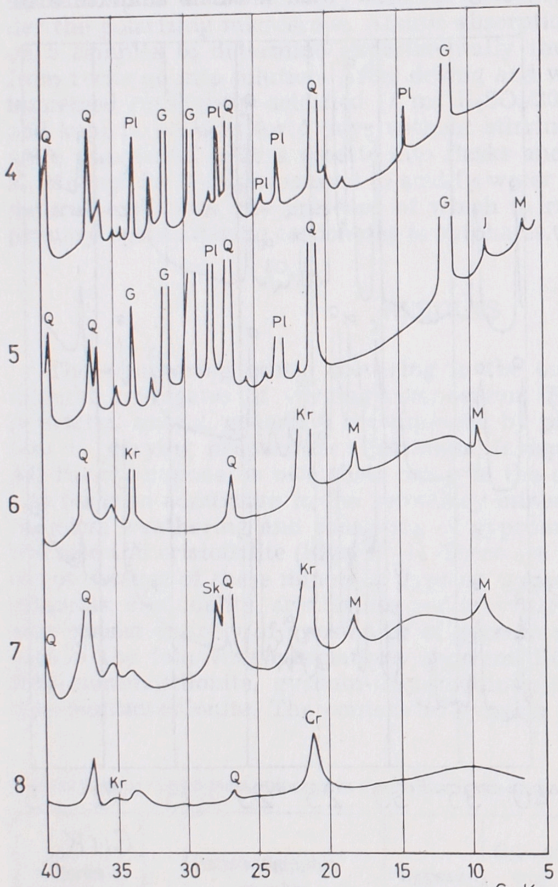
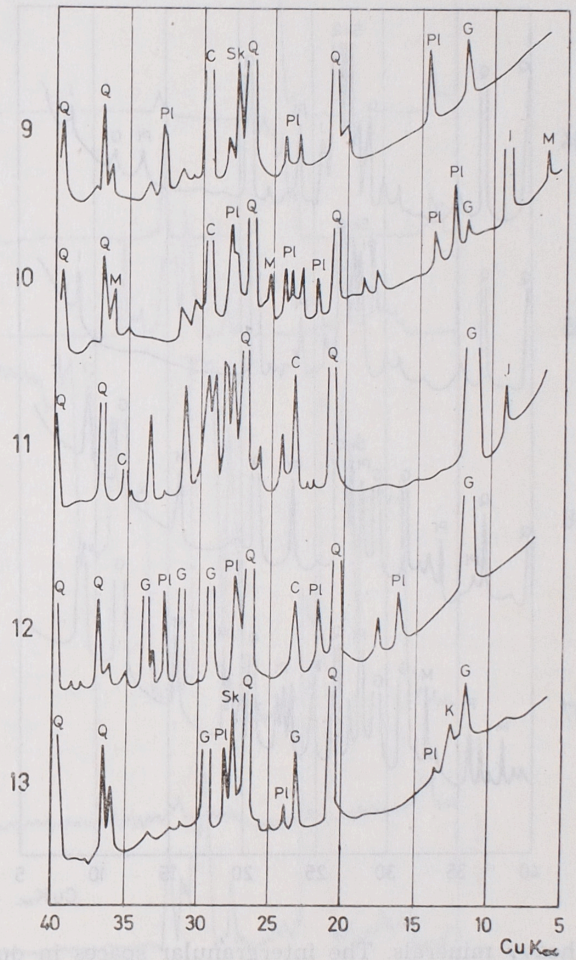


Fig. 2. X-ray diffraction patterns of weathering mineral aggregates of sandstone tors
4 — Beskid Niski Mts near Folusz — „Diabli Kamień" (nature monument), *5* — Beskid Niski Mts — Ruski Zamek near Pielgrzymka, Magura sandstones, *6–8* — Beskid Niski Mts — Góra Zamkowa near Mrukowa, Magura sandstones

te grains. Most feldspar crystals are sharp-edged. Flaky concentrations of micas consist more usually of muscovite than biotite. Carbonate minerals, mainly calcite, appear in varying amounts, principally in intergranular spaces. Heavy minerals (pyroxenes, zircon, rutile, garnet, staurolite) are an accessory component, generally forming inclusions within quartz grains. Opaque minerals are present in varying amounts and diverse forms, either as grains of detrital origin or as syngenetic components (mainly pyrite) or epigenetic weathering minerals. Epigenetic minerals are represented by gypsum, iron hydroxides and clay minerals. Gypsum

concentrates in the intergranular spaces or in the near-surface zones of tors, where it forms aggregate-like concentrations in which single crystals are generally up to 300 μm in size (Phot. 4). Two types of gypsum concentrations have been noted. In the near-surface zones pure aggregate-like concentrations predominate, while in the deeper parts of the rock there

Fig. 3. X-ray diffraction patterns of weathering mineral aggregates of sandstone tors
9–10 — Beskid Niski Mts — Piotruś near Dukla, Mszanka Sandstones (nature monument), *11* — Bieszczady Foreland near Lesko — „Kamień Leski", Krosno sandstone (natural monument), *12* — Beskidy Foreland near Krosno — „Prządki", Ciężkowice sandstones (nature reserve), *13* — Beskidy Foreland near Odrzykoń — Smoczy Dół, Ciężkowice sandstones



are smaller concentrations coloured brown by Fe^{3+} oxides. Iron hydroxides (geothite, lepidocrocite?) appear as impregnating and cementing substances (Phot. 5) which change the colour of some rock-forming minerals. Clay minerals (illite, kaolinite, montmorillonite) form fine flakes in the intergranular spaces, their content being usually insignificant.

Microscopic examination and electron microprobe analysis have revealed that the rock-forming minerals have been subject to epigenetic alteration which can be accounted for by weathering processes.

Quartz grains observed in thin sections often show mosaic or wavy extinction, which testifies to the distortion of their crystal lattice. The grains lying close to the surface of tors are fractured, and microprobe studies have shown that the fractures run parallel to the surface of tor walls. Quartz crystals sometimes contain inclusions of rutile, garnet and other

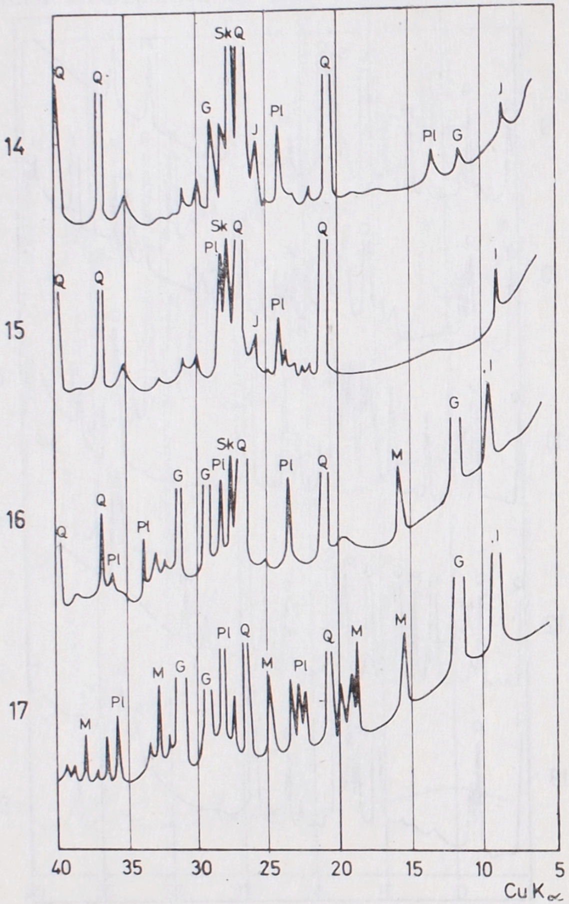


Fig. 4. X-ray diffraction patterns of weathering mineral aggregates of sandstone tors

14—15 — Beskidy Foreland near Muchówka — Kamienie Brodzińskiego, Istebna sandstones (nature monument), *16—17* — Beskidy Foreland near Leksandrowa — „Kamień—Grzyb", Istebna sandstones (nature reserve)

heavy minerals. The intergranular spaces in quartz have expanded and the cement that fills them up has been saturated with secondary iron compounds.

The evidence of alteration of potassium feldspars is provided by lamellar mica concentrations within their grains and by concentrations of fine--flaky clay minerals, mainly illite. In places, quartz-sericite pseudomorphs formed after the weathering decomposition of potassium feldspars. Plagioclases are sometimes accompanied by small concentrations of carbonates (Phot. 6). Plagioclase crystals have undergone structural transformation involving the disappearance of twin striation of the albite type. A large

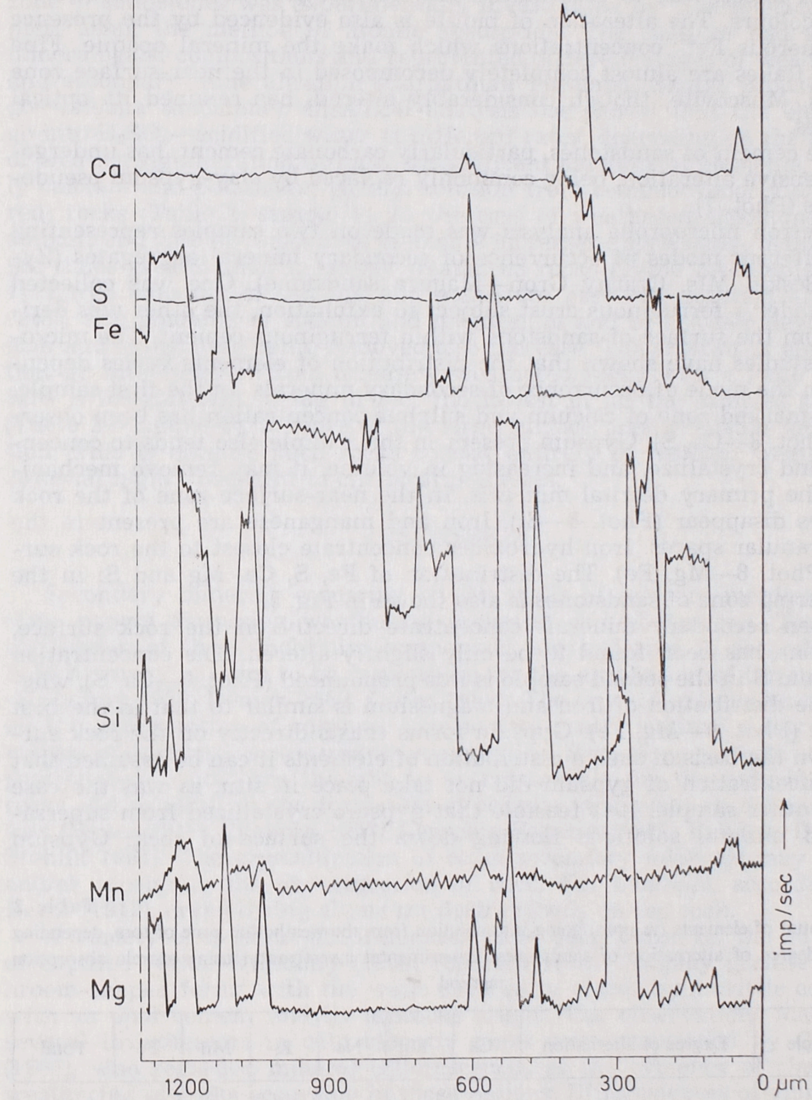


Fig. 5. Linear distribution of Mg, Mn, Si, Fe, S, Ca. Electron microprobe scans from surface deep into the rock. Magura sandstones with secondary mineral crusts. Żywiec Beskid Mts — Czarny Groń

number of feldspar grains show fractures running parallel to the surface of rock.

Fine-flaky secondary clay minerals appear within lamellar concentrations of micas. Due to this, biotite has lost the pleochroism and interference colours. The alteration of biotite is also evidenced by the presence of numerous Fe^{3+} concentrations which make the mineral opaque. Fine biotite flakes are almost completely decomposed in the near-surface zone of tors. Muscovite, though considerably altered, has retained its optical features.

The cement of sandstones, particularly carbonate cement, has undergone extensive alteration, being commonly replaced by clay-gypsum pseudomorphs (Phot. 7).

Electron microprobe analysis was made on two samples representing two different modes of occurrence of secondary mineral aggregates (Żywiec Beskid Mts, Czarny Groń—Magura sandstone). One was collected from under a ferruginous crust subject to exfoliation, the other was derived from the surface of sandstone with a ferruginous cement. The microprobe studies have shown that the distribution of elements varies depending on the mode of occurrence of secondary minerals. In the first sample, a well-marked zone of calcium and sulphur concentration has been observed (Phot. 8—Ca, S). Gypsum present in this sample also tends to concentrate and crystallize, and increasing in volume, it may remove mechanically the primary detrital minerals. In the near-surface zone of the rock silicates disappear (Phot. 8—Si). Iron and manganese are present in the intergranular spaces. Iron hydroxides concentrate closest to the rock surface (Phot. 8—Mg, Fe). The distribution of Fe, S, Ca, Mg and Si in the weathering zone of sandstones is also shown in Fig. 5.

When secondary minerals concentrate directly on the rock surface, sandstone has been found to be only slightly altered. The concentration of Ca and S in the second sample is less pronounced (Phot. 9—Ca, S), whereas the distribution of iron and magnesium is similar to that in the first sample (Phot. 9—Mg, Fe). Gypsum forms crusts directly on the rock surface. On the basis of such a distribution of elements it can be assumed that the concentration of gypsum did not take place in situ, as was the case in the other sample. It is feasible that gypsum crystallized from supersaturated mineral solutions flowing down the surface of rock. Gypsum

Table 2

The amount of elements (in ppm) going into solution from the weathering zone of tors, depending on the degree of alternation of sandstones. Experimental investigation using atomic absorption method

Sample	Degree of alternation	Ca	Mg	Na	K	Mn	Fe	Total
1		30	12	7	35	1	1	86
2	poor	195	30	5	45	1	2	278
3	intermediate	320	17	43	19	2	3	404
4		400	22	10	172	2	2	608
5	intense	20	2	2	5	1	1	31

crusts of this type form near, or more commonly below, the places to which solutions migrate from inside the rock.

The sequence and rate of removal of elements from the weathering zone of sandstones was experimentally investigated for five selected samples, using the method of atomic absorption. The samples had similar mineralogical compositions and represented different stages of weathering and secondary mineralization (Carpathian Foreland, Skałki Brodzińskiego—Istebna sandstone). Chemical analysis has shown that the elements go into H_2SO_4—acidified water at different rates, depending on the degree of weathering alteration of rock. Insignificant amounts of elements, mainly calcium and potassium, go into solution from compact (poorly weathered) rocks (Table 2, sample 1). In the case of weathered sandstones, the amount and rate of removal of elements increases appreciably, being even ten times greater than in poorly weathered rocks (Table 2—samples 2, 3, 4). Large amounts of calcium and potassium pass into solution at rapid rates. The amounts of sodium and magnesium and in a lesser degree, of iron and manganese being romoved also increase. The amount of elements that go into solution from intensely weathered rocks with a loose structure is insignificant, being in fact the lowest of all the samples studied (Table 2—sample 5), in spite of the large surface area available for reaction. This is because such rocks consist entirely of residual weathering material highly resistant to chemical processes.

DISCUSSION

Secondary minerals occurring on the walls of tors are mentioned in some papers discussing weathering processes and phenomena. The crystallization of these indefinite compounds, also referred to as „salts", is held by many authors to be responsible for the exfoliation of tor surfaces (Wilhelmy 1958, Demak 1967, Ollier 1969). The type of exfoliation caused by the precipitation of sub-and near-surface „salt" laminae a few millimeters in thickness is referred to as exudation. Secondary gypsum and the precipitated „salts" are thought to be responsible for the induration of rocks and to assist in the formation of cellular structures on the walls of tors (Beyer 1912; Chabera 1957; Lenschig-Sommer 1960; Czudek, Demek, Stehlik 1961). The crystallization of some secondary minerals may cause and/or accelerate the disintegration of rock. For example, according to Beyer (1912), crystallizing alums act destructively on the rock.

A variety of mineral efflorescences have been found on the surfaces of exposed rocks. Wilhelmy (1958) reported from Uruguay granite mushroom-shaped forms with the walls covered in places by a brittle coating with an opal cement and by siliceous crusts. The observations made by several investigators in cold climatic zones were mentioned by Czeppe (1966), who regarded mineral efflorescences as the evidence of chemical weathering of rocks occurring in those regions. Effloreslences of alum and sulphates (Philippi 1906) as well as mirabilite (Cailleux 1962) were found on the rocks in question. On the walls of sandstone tors occurring within the outcrops of Cretaceous sandstones in Czechoslovakia and Germany, mainly alum-gypsum efflorescences were noted.

First attempts at explaining the genesis of alum-gypsum efflorescences found on sandstones were made by Beyer (1912) and Novak (1914).

These authors put forward independently a hypothesis that rainwater containing sulphur compounds played a significant role in the formation of gypsum and alum .The papers of Lentschig-Sommer (1960, 1961) on the cellular structures (Wabenverwitterung) of sandstone tors of Saxon Switzerland have provided so far most comprehensive data on the chemical mechanism, the mode of occurrence and the role of secondary weathering mineral substances precipitated on the walls of tors. Using laboratory methods, the cited author found that these were alum-gypsum efflorescences and that they assisted in some measure in the formation and development of cellular structures. The chemical reactions giving rise to alum and gypsum involve the action of the decomposition products of sulphide minerals (mainly pyrite) on Ca, Na and K liberated during the decomposition of some rock constituents, primarily feldspars. Alum and gypsum, being readily soluble in water, recrystallize many times, thereby loosening the rock. Lentschig-Sommer (1961) defined the botryoidal alum-gypsum crusts as the mineral alunogen (keramohalite).

The secondary minerals precipitated on the walls of sandstone tors in the Polish Carpathians have not yet been the object of detailed studies (Alexandrowicz 1978 a). Świdziński (1933), an expert on Carpathian tors, reviewed the papers dealing with the genesis of cellular structures of the „Prządki" tors (near Krosno) and found that neither salt efflorescences nor clear evidence of surface cementation was mentioned.

The weathering minerals reported from the Flysch Carpathian sediments are: melanterite, geothite, epsomite, gypsum, jarosite (Kubisz 1958, 1964; Kubisz, Michałek 1959; Badak, Kubisz, Michałek 1962), allophanes (Michałek, Stoch 1958), basaluminite (Wieser 1976) and keramohalite (Tokarski 1905). Sulphates predominate among these minerals, and most of them were found at the surface of clay and clay-siltstone rocks. In the case of rocks with a psammitic or psephitic texture, mainly iron hydroxides and gypsum were noted. According to Kubisz (1958), in rocks containing iron sulphides or subject to the activity of water rich in such compounds, secondary minerals of the alunite-jarosite series are formed. These are microcrystalline potassium, sodium or hydronium aggregates varying in compactness. At the final stage of alteration they become an aggregate consisting of jarosite, quartz, goethite, illite and kaolinite. The commonest forms of occurrence of these minerals are crusts up to a few mm in thickness on the surface of rock or along its cleavage planes, which are generally referred to as alum crusts. Potassium and sodium necessary for their formation are leached from rock-forming minerals. The process leading to the rise of such aggregates, called jarositization, operates primarily in the rock cement, resulting in its replacement by a friable secondary substance subject to crystallization.

The pricipal epigenetic mineral of the Polish Flysch Carpathian tors is gypsum. It forms during the decomposition of rock-forming minerals, the process being assisted by atmospheric agents. Liberated sulphur and calcium are necessary for the rise of gypsum, and the chemical reactions involved may proceed in the following way.

$$SO_2+\frac{1}{2}O_2 \longrightarrow SO_3$$

$$SO_3+H_2O \longrightarrow H_2SO_4$$

$$CaCO_3+H_2SO_4+2\,H_2O \longrightarrow CaSO_4\cdot 2\,H_2O+H_2CO_3$$

Electron microprobe studies of the outermost zones of weathered sandstones have revealed the presence of sulphur (Phots. 8, 9—S). It presumably comes mostly from the atmosphere, where it is now widespread in varying concentrations as SO_2. Sulphur dioxide reacts with rainwater to form sulphuric acid which acts on the exposed rock, causing the slow decomposition of its alkaline rock-forming minerals and leading to the formation of new compounds of the sulphate group. Sulphur may also be liberated from the weathering sulphides, e.g. pyrite or marcasite, present in sandstones, yet it is mainly iron sulphates, e.g. melanterite, that form in this process.

Calcium may be the product of decomposition of both calcite and plagioclases. Recrystallized calcite is present in the cement of sandstones, and during the weathering of rocks it is the cement constituents that are leached and liberated in the first place. Electron microprobe spectra reveal the presence of calcium in the outermost or weathered zones of sandstone tors (Phots. 8, 9—Ca). Compared with other elements, calcium from poorly and moderately weathered rocks goes into solution in large amounts and at a rapid rate (Table 2). That calcium originated from the decomposition of plagioclases is evidenced by small concentrations of carbonates accompanying plagioclase crystals with a partly obliterated structure (Phot. 6).

Another group of epigenetic minerals of Carpathian sandstone tors is represented by clay minerals: illite, kaolinite and montmorillonite. They owe their origin to the alteration of potassium feldspars and micas, mainly biotite. This is evidenced by the concentrations of fine—flaky clay minerals noted on potassium feldspars and within micas. The genesis of clay minerals may also be associated with the epigenetic alteration of marly cement of sandstones, which is locally replaced by clay-gypsum pseudomorphs (Phot. 7).

The occurrence of epigenetic cristobalite is confined to very few localities (Beskid Niski Mts near Mrukowa—Magura sandstone). The samples collected so far require further studies to determine the chemical processes that led to the formation of this mineral.

The common weathering phenomena occurring in sandstones under the influence of atmospheric agents are the oxidation and hydration of iron. Iron hydroxides which form in these processes impart the brown-red colour to the rock. They are present in varying amounts in the intergranular spaces, concentrating as a rule in the near-surface zones (Phots. 8, 9—Fe). Crusts of this type are not chemically homogeneous. They are aggregates consisting of detrital, mainly quartz grains, various secondary minerals and iron hydroxides generally represented by goethite. They form a separate group of secondary weathering minerals, similar in the form of occurrence to the alunite-jarosite series discussed by Kubisz (1958, 1964) but differing from the latter in the chemical composition. Further studies will certainly throw light on the genesis of cristobalite as yet another secondary mineral associated with the węathering of some sandstones. Also the successive stages of alteration of the already formed secondary minerals and the part they play in the natural destruction of tors have not yet been accounted for.

The precipitation of secondary minerals promotes the disintegration of sandstones. The mechanical removal of detrital minerals takes place in those parts of the rock where epigenetic gypsum crystallizes, because this mineral has a great force of recrystallization, and thereby the ability to expand. Epigenetic minerals concentrate in the near-surface zone of the rock and loosen its structure. The rock-forming mineral grains of this zone are fractured parallel to the rock surface. The disintegration of quartz, manifesting itself in the fracturing of grains and the expansion of intergranular spaces, has been observed during the weathering of granitic rocks as a result of an early stage of chemical corrosion (Stoch, Helios-Rybicka 1975). According to these authors, further disintegration of quartz grains is expedited by the crystallization of new minerals in the intergranular fissures. In sandstones exposed as tors and subject to the action of atmospheric agents for a long time, the parallel fractures in rock-forming grains may also have been produced by relief forces and by repeated diurnal and seasonal changes in thermal conditions. These fractures often provide channels for migration of solutions and become a locus for the precipitation of secondary minerals which accelerate further disintegration of the rock.

The structure of the external zones of sandstone tors is affected both by the precipitation of secondary minerals and the mode of fracturing of detrital grains. The main lines of looseness of rock run parallel to its surface. It is feasible, therefore, that there is a close genetic relation between the surface microexfoliation of tors and the decomposition of sandstones produced by chemical weathering. This thesis is also borne out by direct observations of the near-surface zones of tors, as the rock is readily detached in places where mineral crusts are present. The detachment is particularly likely to occur when secondary minerals concentrate in the sub-surface zones of sandstones, or when they impregnate the surface layer. The precipitation of mineral crusts directly on the rock surface promotes its breaking and disintegration into separate grains because in these places the sandstone is considerably depleted in cement.

Translated by Hanna Kisielewska

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NASKORUPIENIA SUBSTANCJI EPIGENETYCZNYCH POWIERZCHNIOWEJ STREFY WIETRZENIA SKAŁEK PIASKOWCOWYCH W KARPATACH POLSKICH

Streszczenie

Oryginalnymi i rzadko spotykanymi formami rzeźby Karpat fliszowych są różnopostaciowe skałki piaskowcowe i zlepieńcowo-piaskowcowe (fot. 1). Są one szczególnie dogodne do studiowania procesów wietrzenia jako naturalne odsłonięcia pozostające przez długi czas pod działaniem czynników atmosferycznych, zarówno w zimnej strefie peryglacjalnej Würmu jak również w umiarkowanym klimacie holocenu. Jednym z przejawów wietrzenia chemicznego utworów skałek są wtórne agregaty mineralne wytrącające się lokalnie w postaci naskorupień bezpośrednio na powierzchni

ścian lub w strefach przypowierzchniowych (fot. 2). Skupienia substancji mineralnych na ogół o zabarwieniu białym lub jasnoszarym, mają różną spoistość, od odmian twardych i szklistych do miękkich rozpadających się na proszek. Agregaty są zanieczyszczone ziarnami detrytycznymi, głównie kwarcu. Badaniami rentgenowskimi wyróżniono 5 rodzajów epigenetycznych substancji mineralnych reprezentowanych przez gips, gips i minerały ilaste, minerały ilaste, krystobalit oraz krystobalit i minerały ilaste (fig. 1—4, tabl. 1). Wśród minerałów ilastych rozpoznano illit, kaolinit i montmorillonit. Wymienione minerały epigenetyczne nie były dotychczas opisywane ze skałkowych, piaskowcowych warstw fliszu karpackiego. W innych obszarach skałkowych, a zwłaszcza Saskiej Szwajcarii, były rozpoznane ałuny i gips.

W celu wyjaśnienia pochodzenia wtórnych minerałów posłużono się badaniami mikroskopowymi płytek cienkich fragmentów piaskowców w obrębie których występowały naloty mineralne, wykonano analizy przy użyciu mikrosondy elektronowej oraz metodą absorpcji atomowej (fot. 3—9, fig. 5, tabl. 2). Uzyskane wyniki świadczą o przeobrażeniu w różnym stopniu minerałów skałotwórczych przypowierzchniowych stref skałek. Zaznacza się ono zmianami chemizmu utworów (przez wydzielenia minerałów wtórnych i pseudomorfozy), koncentracją niektórych pierwiastków oraz deformacją kryształów polegającą głównie na spękaniu ziarn równolegle do powierzchni skały. Wytrącanie się minerałów wtórnych jest wynikiem chemicznego rozkładu, pod wpływem czynników atmosferycznych, niektórych składników detrytycznych oraz spoiwa piaskowców i zlepieńców. Podlegają temu zwłaszcza plagioklazy, skalenie, kalcyty i łyszczyki. W tworzeniu się gipsu — najpospolitszego minerału naskorupień, duży udział ma woda opadowa zawierająca związki siarki.

Proces wytrącania się minerałów wtórnych sprzyja naturalnemu niszczeniu skałek, doprowadzając do rozluźnienia struktury ich utworów. W miejscach obfitego występowania substancji epigenetycznych powierzchnie skałek łatwo ulegają eksfoliacji.

OBJAŚNIENIA DO FIGUR

Fig. 1. Dyfraktogramy rentgenowskie wietrzejących agregatów mineralnych z powierzchni skałek piaskowcowych
G — gips, I — illit, K — kaolinit, M — montmorillonit, Cr — krystobalit, Q — kwarc, Pl — plagioklaz, Sk — skaleń potasowy, C — kalcyt. *1* — Beskid Żywiecki — Czarny Groń, piaskowce magurskie, *2* — Beskid Żywiecki, — Weska, piaskowce magurskie, *3* — Beskid Wyspowy — Luboń Wielki, piaskowce magurskie (rezerwat przyrody)

Fig. 2. Dyfraktogramy rentgenowskie wietrzejących agregatów mineralnych z powierzchni skałek piaskowcowych
4 — Beskid Niski koło Folusza, „Diabli Kamień", piaskowce magurskie (pomnik przyrody), *5* — Beskid Niski, Ruski Zamek koło Pielgrzymki, piaskowce magurskie, *6—8* — Beskid Niski — Góra Zamkowa koło Mrukowej, piaskowce magurskie

Fig. 3. Dyfraktogramy rentgenowskie wietrzejących agregatów mineralnych z powierzchni skałek piaskowcowych
9—10 — Beskid Niski — Piotruś koło Dukli, piaskowce z Mszanki, *11* — Przedgórze Bieszczadzkie koło Leska — „Kamień Leski", piaskowce krośnieńskie (pomnik przyrody), *12* — Pogórze Beskidzkie koło Krosna — „Prządki" (rezerwat przyrody), Piaskowce ciężkowickie, *13* — Pogórze Beskidzkie koło Odrzykonia — Smoczy Dół, piaskowce ciężkowickie

Fig. 4. Dyfraktogramy rentgenowskie wietrzejących agregatów mineralnych z powierzchni skałek piaskowcowych
14—15 — Pogórze Beskidzkie koło Muchówki — „Kamienie Brodzińskiego" piaskowce istebniańskie (pomnik przyrody), *16—17* — Pogórze Beskidzkie koło Leksandrowej, „Kamień—Grzyb" piaskowce istebniańskie (rezerwat przyrody)

Fig. 5. Wykresy zmienności liniowej zawartości Mg, Mn, Si, Fe, S, Ca od powierzchni skały w głąb. Piaskowce mineralne z wtórnymi naskorupieniami mineralnymi, Beskid Żywiecki — Czarny Groń (mikrosonda elektronowa)

OBJAŚNIENIE FOTOGRAFII

Fot. 1. Skałki w rezerwacie przyrody „Prządki" koło Krosna
Fot. 2. Epigenetyczny, drobnokrystaliczny gips obrastający ziarna detrytyczne piaskowca na powierzchni ścian „Skałek Brodzińskiego"
Fot. 3. Fragment metapiaskowca. Piaskowce istebniańskie, „Skałki Brodzińskiego". Pow. 34×, nikole X
Fot. 4. Koncentracje drobnokrystalicznego gipsu w przypowierzchniowych strefach piaskowca istebniańskiego „Skałek Brodzińskiego". Pow. 34×, nikole X
Fot. 5. Koncentracje wodorotlenków żelaza w przestrzeniach międzyziarnowych przypowierzchniowej strefy piaskowca istebniańskiego „Skałek Brodzińskiego". Powiększenie 34×, 1 nikol
Fot. 6. Ziarno średniozasadowego plagioklazu ulegające procesom przeobrażeniowym związanym z odprowadzeniem Ca. Pow. 34×, nikole X
Fot. 7. Pseudomorfoza ilasto-gipsowa po spoiwie węglanowym. Powiększenie 34×, nikole X
Fot. 8. Rozmieszczene pierwiastków Fe, S, Ca, Mg, Si w piaskowcu magurskim (Beskid Żywiecki—Czarny Groń) zawierającym wtórne substancje mineralne w strefie podpowierzchniowej.
T — Topografia powierzchni piaskowca.
Mikrosonda elektronowa. Pow. 125×
Fot. 9. Rozmieszczenie pierwiastków Fe, S, Ca, Mg w piaskowcu magurskim (Beskid Żywiecki—Czarny Groń) zawierającym wtórne substancje mineralne bezpośrednio na powierzchni.
T — Topografia powierzchni piaskowca.
Mikrosonda elektronowa. Pow. 125×

Зофья АЛЕКСАНДРОВИЧ Мацей ПАВЛИКОВСКИ

СКОРЛУПЧАТЫЕ ОБРАЗОВАНИЯ ЭПИГЕНЕТИЧЕСКИХ ВЕЩЕСТВ КОРЫ ВЫВЕТРИВАНИЯ ПЕСЧАНИКОВЫХ ОСТАНЦЕВ В ПОЛЬСКИХ КАРПАТАХ

Резюме

Своеобразными и редко встречаемыми формами рельефа флишевых Карпат являются разнообразные песчаниковые и конгломератово-песчаниковые останцы (фото 1). Они особенно пригодны для изучения процессов выветривания — в качестве естественных обнажений, длительное время подверженным воздействии атмосферных факторов как в холодной перигляциальной зоне Вюрма, так и в умеренном климате голоцена. Одним из проявлений химического выветривания скальных образований являются вторичные минеральные агрегаты, отлагающиеся местами в виде скорлуп непосредственно на поверхностях стен, или в приповерхностных зонах (фото 2). Скопления минерального вещества, обычно белого или светлосерого цвета, характеризуются различной

компактностью — от твердых и стекловидных до мягких, рассыпающихся в порошок, разновидностей. Агрегаты загрязнены обломочными зернами, главным образом кварца. Рентгеновскими исследованиями выделены 5 родов эпигенетических минеральных веществ, представленных гипсом, гипсом и глинистыми минералами, кристобалитом, а также кристобалитом и глинистыми минералами (фиг. 1—4, табл. 1). Среди глинистых минералов определены иллит, каолинит и монтмориллонит. Упомянутые эпигенетические минералы в останцевых, песчаниковых слоев карпатского флиша до сих пор не описывались. В других областях развития скал, в частности в Саской Щвайцарии, были найдены квасцы и гипс.

С целью выяснения происхождения вторичных минералов проводилось микроскопическое изучение прозрачных шлифов тех фрагментов песчаников, в пределах которых наблюдались минеральные налеты, проводились анализы на микрозонде, а также атомноабсорбционным методом (фото 3—9, фиг. 5, табл. 2). Полученные результаты свидетельствуют о различной степени преобразования породообразующих минералов в приповерхностных зонах скал. Оно обозначается изменением химизма образований (через выделение вторичных минералов и псевдоморфозы), концентрацией некоторых химических элементов, а также деформацией зерен, в основном заключающейся в образовании трещин в зернах, параллельно к поверхности скалы. Отложение вторичных минералов является следствием химического разложения под воздействием атмосферных факторов некоторых обломочных компонентов. В частности этому подвергаются плагиоклазы, калишпаты, кальцит и слюды. В образовании гипса — наиболее распространенного минерала скорлуп — большая роль приходится на воды из осадков, содержащие соединения серы.

Процесс отложения вторичных минералов благоприятствует естественному разрушению останцев, приводя в ослаблению структуры их образований. В местах обильного развития эпигенетического вещества поверхности скал легко расслаиваются.

ОБЪЯСНЕНИЯ К ФИГУРАМ

Фиг. 1. Рентгеновские дифрактограммы минеральных агрегатов из зоны выветривания на поверхности песчаниковых останцев

G — гипс, M — монтмориллонит, Cr — кристобалит, I — иллит, K — каолинит, Q — кварц, Pl — плагиоклаз, Sk — калишпат, C — кальцит.

1 — Живецкий Бескид — Чарны Гронь, магурские песчаники, *2* — Живецкий Бескид — Вэска, магурские песчаники, *3* — Высповый Бескид — Любонь Вельки, магурские песчаники (природный заповедник)

Фиг. 2. Рентгеновские дифрактограммы минеральных агрегатов зоны выветривания на поверхности песчаниковых останцев

4 — Низкий Бескид около Фолюша — «Дябли Камень», магурские песчаники (природный заповедник), *5* — Низкий Бескид — Руски Замэк около Пельгжимки, магурские песчаники, *6—8* — Низкий Бескид — Гура Замкова около Мруковы, магурские песчаники

Фиг. 3. Рентгеновские дифрактограммы минеральных агрегатов зоны выветривания на поверхности песчаниковых останцев

9—10 — Низкий Бескид — Пётрусь около Дукли, песчаники из Назанки, *11* — Бещадское предгорье около Леска — «Камень Легки», кросноские песчаники (природный заповедник), *12* — Бескидское нагорье около Кросна — «Пшондки» (природный заповедник), циенжковицкие песчаники, *13* — Бескидское нагорье около Оджиконя — Смочи Дул, циенжковицкие песчаники

Фиг. 4. Рентгеновские дифрактограммы минеральных агрегатов зоны выветривания на поверхности песчаниковых останцев

14—15 — Бескидское нагорье около Мухувки — «Камене Бродзиньского», истэбнанские песчаники (памятник природы), *16—17* — Бескидское нагорье около Лександровы — «Камень Гжиб», истэбнанские песчаники (природный заповедник)

Фиг. 5. Графики линейной изменчивости содержания Mg, Mn, Si, Fe, S, Ca от поверхности в глубь породы. Магурские песчаники с вторичными минеральными образованиями скорлуп. Живецкий Бескид — Чарны Гронь (по микрозонду)

ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

Фото 1. Останцы в природном заповеднике «Пшондки» около Кросна

Фото 2. Эпигенетический мелкокристаллический гипс, обрастающий детритовые зерна песчаника на поверхности стен «Скалок Бродзиньского»

Фото 3. Фрагмент метапесчаника. Истэбнанские песчаники, «Скалки Бродзиньского». Увел. × 34, скрещенные николи

Фото 4. Концентрации мелкокристаллического гипса в приповерхностных зонах истэбнанского песчаника «Скалок Бродзиньского». Увел. × 34, скрещенные николи

Фото 5. Концентрации гидроокислов железа в межзерновых пустотах приповерхностной зоны истэбнанского песчаника «Скалок Бродзиньского». Увел. × 34, один николь

Фото 6. Зерно умеренной основности плагиоклаза, подвергающееся преобразовательным процессам, связанным с выносом Ca. Увел. × 34, скрещенные николи

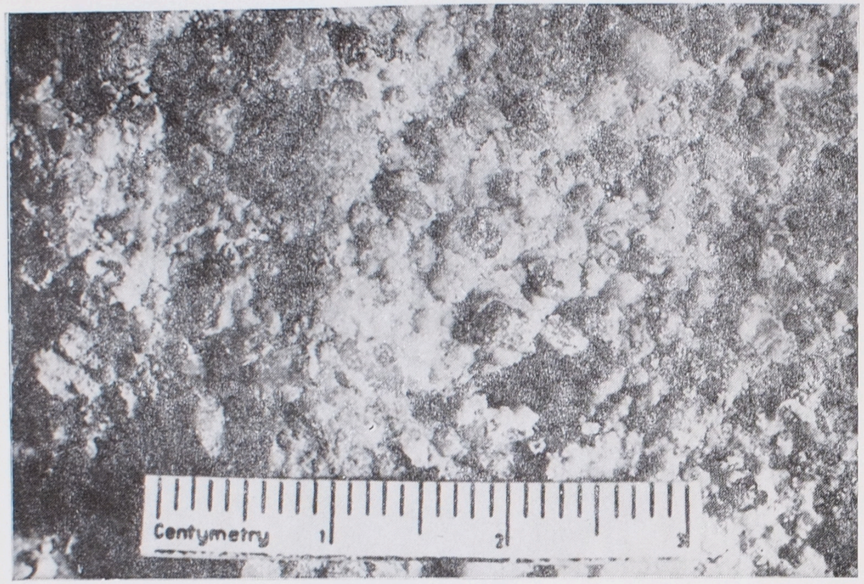
Фото 7. Глинисто-гипсовая псевдоморфоза по карбонатном цементе. Увел. × 34, скрещенные николи

Фото 8. Распределение Fe, S, Ca, Mg, Si в магурском песчанике (Живецкий Бескид — Чарны Гронь), содержащим вторичные минеральные вещества в подповерхностной зоне. T — топографическое изображение поверхности песчаника. Микрозонд. Увел. × 125

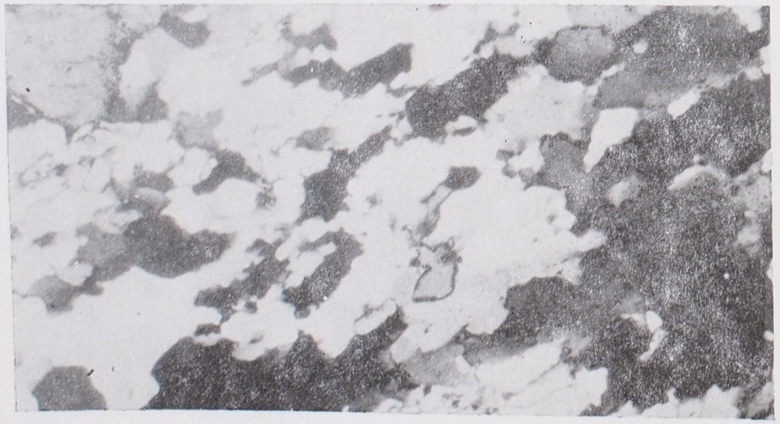
Фото 9. Распределение Fe, S, Ca, Mg в магурском песчанике (Живецкий Бескид — Чарны Гронь), содержащим вторичные минеральные вещества непосредственно на поверхности

T — топографическое изображение поверхности песчаника — Микрозонд. Увел × 125

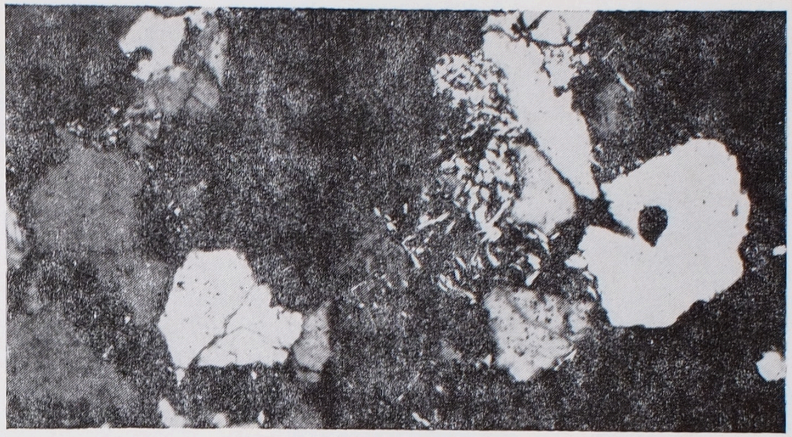
Phot. 1. „Prządki" tors in the nature reserve near Krosno



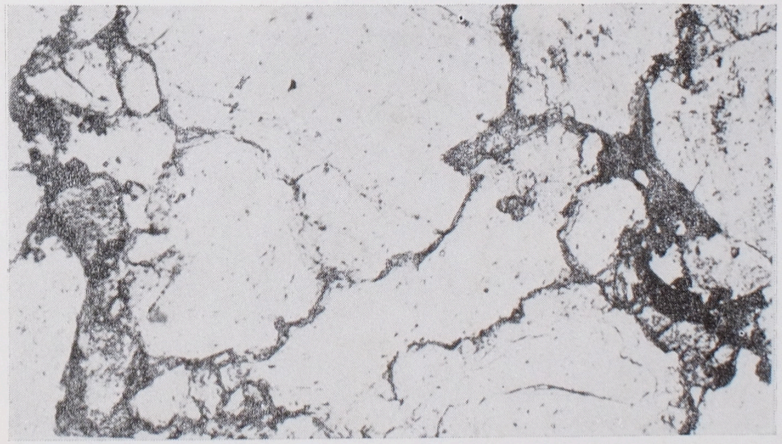
Phot. 2. Epigenetic fine-crystalline gypsum growing on detrital grains of sandstone on the surface of Skałki Brodzińskiego tors



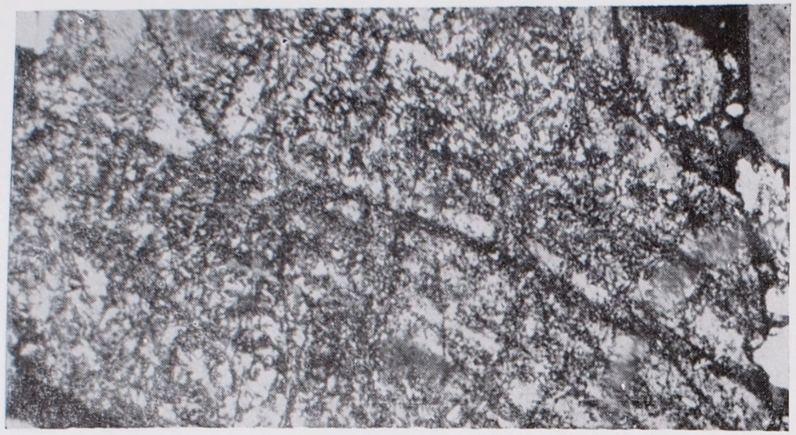
Phot. 3. A fragment of metasandstone. Istebna sandstones, Skałki Brodzińskiego tors. Crossed nicols, 34×



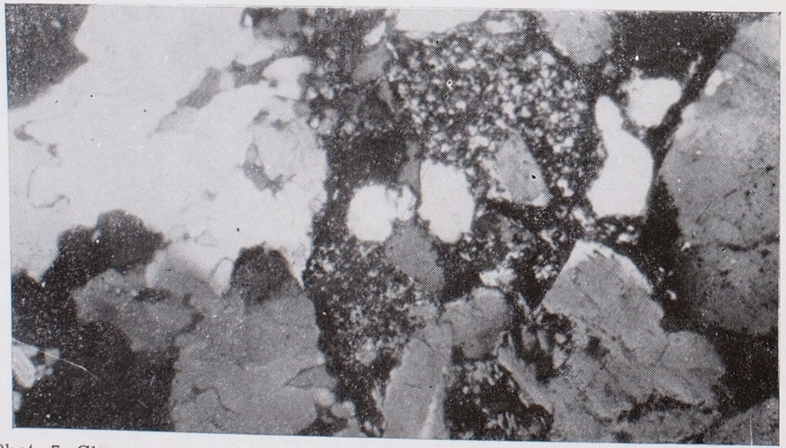
Phot. 4. Fine-crystalline gypsum concentrations in the near-surface zones of Istebna sandstones, Skałki Brodzińskiego tors. Crossed nicols, 34×



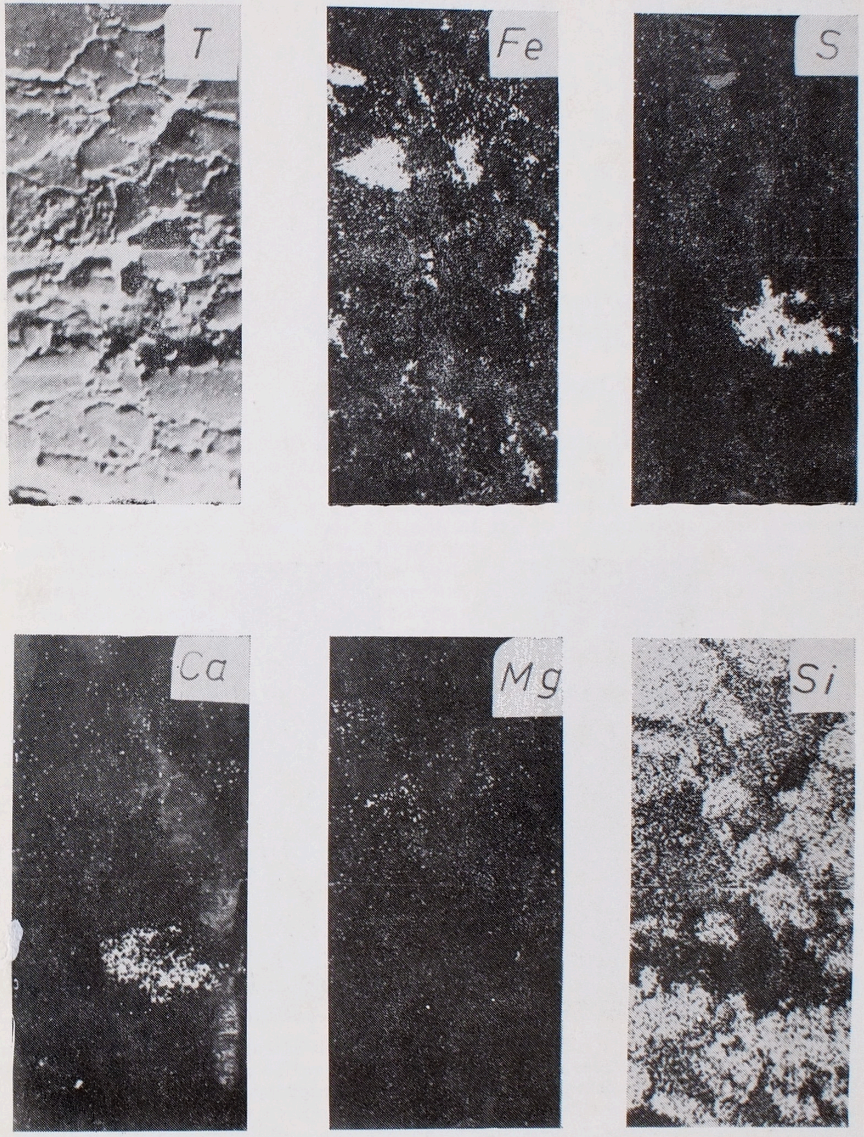
Phot. 5. Iron hydroxide concentrations in intergranular spaces of the near-surface zone of Istebna sandstone. Skałki Brodzińskiego tors. 1 nicol, 34×



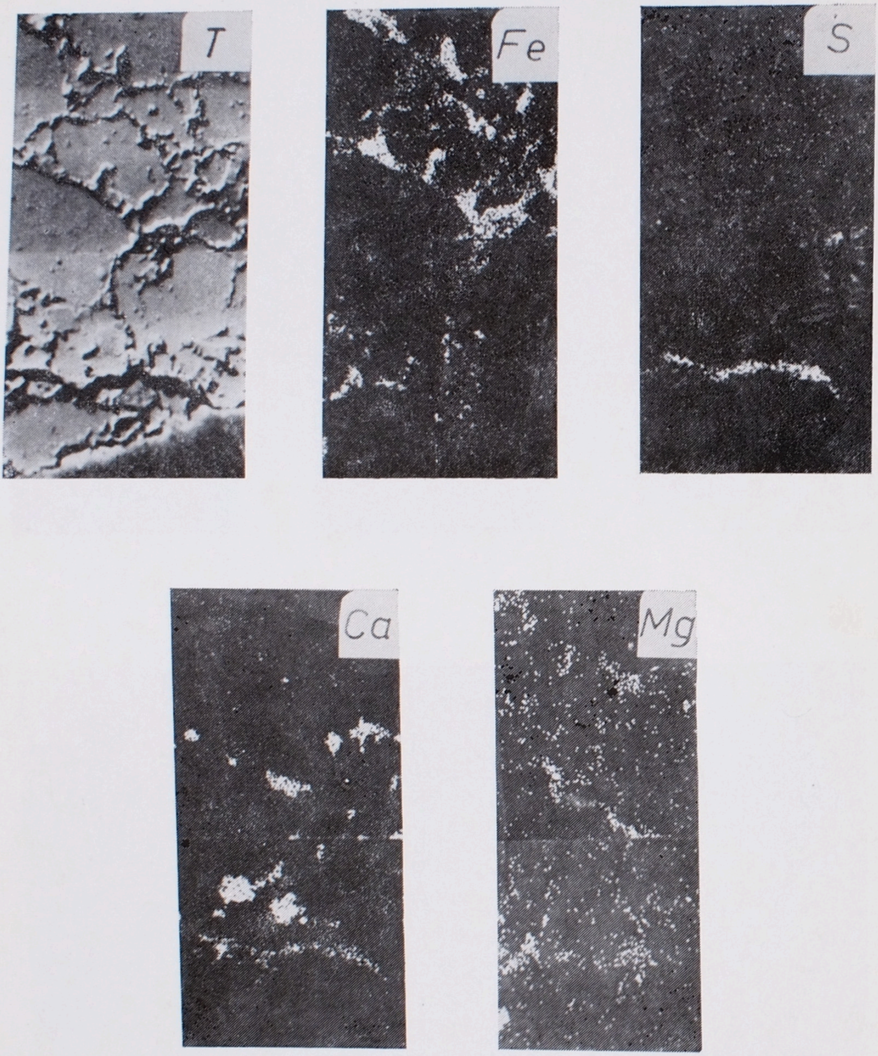
Phot. 6. A grain of medium-basic plagioclase subject to alteration due to the removal of Ca. Crossed nicols, 34×



Phot. 7. Clay-gypsum pseudomorph after carbonate cement. Crossed nicols, 34×



Phot. 8. Fe, S, Ca, Mg, Si distribution in the Magura sandstone (Żywiec Beskid Mts — Czarny Groń) containing secondary minerals in the sub-surface zone. T — topography of sandstone surface. Electron microprobe, 125×



Phot. 9. Fe, S, Ca, Mg distribution in the Magura sandstone (Żywiec Beskid Mts — Czarny Groń) containing secondary minerals directly on the surface. T — topography of sandstone surface. Electron microprobe, 125×