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CHARACTERISTICS OF ACCESSORY MINERALS IN THE SELECTED SAMPLES OF THE WEST CARPATHIAN GRANITOIDS

Tab. 1

The integrated investigation of the selected samples of the West Carpathian granitoids comprises a study of accessory minerals separated from the crushed rocks by the so-called heavy-fraction method. This method consisting of crushing, grinding, sieving, heavy-liquid separation, and separation using a hand- and electromagnet, as applied to the accessory minerals of the Malé Karpaty Mts. granitoids, was published by J. Veselský — M. Žabka (1976). Quantitative evaluation was made according to the method of V. V. Ljachovič — D. A. Rodionov (1961), which expresses the representation of individual accessories in g t of the rock.

With regard to the present knowledge, the data can be generalized on the basis of characteristic assemblages and individual minerals, their mineralogical features and quantitative representation for both the Tatríde, Veporíde and Gemeríde crystalline complexes and for some principal types of the granitoid rocks.

Division of the sample set according to the basic West Carpathian tectonic zones (Tatrídes, Veporídes, Gemerídes) was chosen for the present stage of examination of results. Further successive obtained of mineralogical and geochemical data from the study of accessory minerals enables to evaluate the common features and dependences, or important differences with regard to a division of the West Carpathian crystalline complex, as it is given in the presented work by L. Kamenický or B. Cambel — E. Walzel. According to this division the Tatríde region of core mountains is divided into the West Slovakian (A), North Slovakian (B) and Central Slovakia (C) regions, and Veporídes (D) and Gemerídes (E) crystalline complexes are divided in relatively more detailed way.

The granitoids of the Tatríde crystalline complex are characterized on the grounds of the largest set of samples. The relatively varied assemblage of the accessory minerals can be divided according to chemistry as follows:

- | | |
|----------------|--|
| 1. Sulphides: | pyrite, arsenopyrite, cinnabar, molybdenite, galena |
| 2. Fluorides: | fluorite |
| 3. Oxides: | magnetite, limonite-goethite, ilmenite, rutile, hematite, magnetic nodules, anathase, cassiterite, corundum |
| 4. Carbonates: | calcite, siderite |
| 5. Sulphates: | barite |
| 6. Phosphates: | apatite, monazite, xenotime |
| 7. Silicates: | zircon, garnet (almandine, spessartite, andradite, grossular), sphene, allanite, tourmaline, topaz, hornblende, pyroxene, epidotezoisite, andalusite, sillimanite. |

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This division shows that silicates and oxides are most widely represented minerals.

A different picture of the distribution of accessory minerals is provided by the scheme of the frequency of occurrence according to the classification of V. V. Ljachovič (1973):

1. constantly present minerals — have been identified in 90–100 ‰
from the total number of the samples studied,
2. frequently present — 70–90 ‰,
3. commonly present — 30–70 ‰,
4. rarely present — 10–30 ‰,
5. very rarely present — 0–10 ‰.

The order of the accessory minerals in the Tatríde granitoids, based on this classification, is given in Table 1.

From the results of the study so far performed, the following association of constantly present accessories in the selected granitoid population of the Tatríde region has been deduced: ZIRCON — APATITE — MONAZITE — MAGNETITE — PYRITE — LIMONITE — GOETHITE — EPIDOTE — ZOISITE.

From the standpoint of the quantitative representation of minerals (g t) there are some differences in the typical associations of some rock types in the individual core mountain ranges.

It should be emphasized that the essential differences in the associations of accessory minerals are not systemically dependent on the petrographical division of rocks, accepted for the evaluation of the selected West Carpathian rock samples. The differences rather reflect the general development of the rock in a certain area and thus lend support to the opinion that the accessory minerals were crystallizing during the whole genetic history of the granitoid rocks.

Remarkable in the association of accessory minerals of the Tatríde granitoids is the frequency of monazite occurrence (90–100 ‰), which together with the frequent allanite (70–90 ‰) indicate the enrichment of this rock type in elements of rare earths. The association of the TR elements is complemented by the scarce xenotime (10–30 ‰). A relatively frequent mineral in the West Carpathian granitoids is the late-magmatic metamictic zircon, which contains not only higher U and Hf but also an increased amount of TR elements. The late-magmatic monazite is distinguished by a higher content of U and the U — Th silicates, not precisely identified, forming inclusions in zircons, apatite, monazite and xenotime. The study has also confirmed the occurrence of epidotes with an increased content of TR elements; in this case it is probable that allanite — epidote constitute a continuous isomorphous series. The epidote, however, for the most part envelops allanite and there is a sharp boundary between them both in colour and content of TR elements.

The mineralogical evaluation clearly shows a quantitative predominance and constant occurrence of two geochemical groups:

Ca (Ti)phosphates and silicates:

apatite, monazite, sphene, allanite, epidote-zoisite;

oxides and sulphides of Fe (Ti):

magnetite, ilmenite, pyrite, limonite-goethite.

Table 1
Frequency of occurrence of accessory minerals in the granitoids of the Tatríde crystalline complex

	0	10	30	70	90	100%
ZIRCON	+	+	+	+	+	+
APATITE	+	+	+	+	+	+
MAGNETITE	+	+	+	+	+	+
PYRITE	+	+	+	+	+	+
LIMONITE-	+	+	+	+	+	+
GOETHITE	+	+	+	+	+	+
EPIDOTE-	+	+	+	+	+	+
ZOISITE	+	+	+	+	+	+
MONAZITE	+	+	+	+	+	+
GARNET	+	+	+	+	+	+
ILMENITE	+	+	+	+	+	+
SPHENE	+	+	+	+	+	+
ALLANITE	+	+	+	+	+	+
HORNBLende	+	+	+	+	+	+
LEUCOXENE	+	+	+	+	+	+
RUTILE	+	+	+	+	+	+
XENOTIME	+	+	+	+	+	+
HEMATITE	+	+	+	+	+	+
magn. nodules	+	+	+	+	+	+
ANATASE	+	+	+	+	+	+
TOURMALINE	+	+	+	+	+	+
calcite	+	+	+	+	+	+
PYROXENE	+	+	+	+	+	+
ARSENOPYRITE	+	+	+	+	+	+
CASSITERITE	+	+	+	+	+	+
siderite	+	+	+	+	+	+
CARBONATES	+	+	+	+	+	+
andradite	+	+	+	+	+	+
grossular	+	+	+	+	+	+
SILLIMANITE	+	+	+	+	+	+
BARITE	+	+	+	+	+	+
CINNABAR	+	+	+	+	+	+
ANDALUSITE	+	+	+	+	+	+
TOPAS	+	+	+	+	+	+
CORUNDUM	+	+	+	+	+	+
FLUORITE	+	+	+	+	+	+
MOLYBDENITE	+	+	+	+	+	+
GALENA	+	+	+	+	+	+

The prominent predominance of Ca-accessories is often a result of the presence of the minerals of the epidote-zoisite group. The content of the accessory minerals apatite, sphene, allanite, magnetite, pyrite, ilmenite, epidote-zoisite rises with the basicity of the granitoids, which confirms the prevalently granodiorite to tonalite character (in the sense of IUGS classification) of the West Carpathian granitoid rocks. But, although the content of Fe—Ti oxides — magnetite and ilmenite — strikingly decreases, or ilmenite is absent in relatively more acid varieties, apatite almost invariably predominates over all other accessories. This finding corroborates a more abrupt decrease of Fe and Ti contents in relation to Ca during crystallization differentiation, and a longer lasting crystallization capacity of apatite. The relative decrease in absolute apatite contents is explicable by crystallization of accessory phosphates (monazite, xenotime) in the more acid differentiates of granitoid magma, which enhance the consumption of phosphorus.

We have frequently identified magnetite with a higher Ti content (Ti-magnetite) and exsolutions of the solid phase of ilmenite in magnetite, although these magnetites are not in association with the altered biotite and are regarded as primarily magmatic. It is well known that in chloritization of biotite the secondary sphene, rutile and magnetite are formed to the detriment of exsolved Fe and Ti. In the relatively basic granitoid types of the West Carpathians the high content of epidote is usually accompanied with increased sphene. In such cases the genesis of sphene (in association with altered biotite) is interpreted as a product of secondary alteration of biotite. The last generation of sphene is a product of leucogenization of ilmenite, frequently combined with carbonates, feldspars and or apatite and zircon, which are most likely the primary inclusions in ilmenite. The Ti-mineralization in the association of accessory minerals is complemented by common rutile and rare anatase, which are typical hypogene minerals. It is above all rutile-nigrine which together with other pneumatolytic-magmatic minerals (cassiterite, topaz, molybdenite, fluorite, tourmaline and arsenopyrite) indicates a plausible greisenization of the rock (the Malá Fatra Mts. — ZK 97, 98, 99; the Nizke Tatry Mts — ZK 4. Rutile and anatase have also been established as secondary minerals — sagenite in biotite and anatase as a component of leucogene (s. l.).

Particular attention has been devoted to zircon not only because of its constant occurrence but with regard to its applicability to geochronological purposes. From this point of view, the recognition of the existence of several generations of zircon markedly differing in mineralogico-geochemical properties in almost every sample examined is of great importance. A significant mineralogical feature of late-magmatic — metamictic zircons is the presence of rounded "old" nuclei, i. e. of zircons without any sign of metamictization; their origin may be linked with the paracrystalline rocks. The first-generation (protomagmatic) zircons often show rounded crystal edges, which is ascribed to magmatic corrosion. Marked irregular round forms on the uneven faces of strongly metamictized zircon — cyrtolite from the aplitoid-pegmatitoid granitoid varieties (Suchý, Branisko) are interpreted as due to the effects of late pneumatomagmatic and metasomatic processes. During these processes the "aggressive" solutions are thought to have distorted the surface and partly also the interior of structurally weakened crystals. In cyrtolites and late magmatic-metasomatic zircons the U and Hf content increases, and with the decrease of Zr the Zr/Hf

ratio decreases abruptly. The distribution of these elements in metamictic zircons is very inhomogeneous owing to metamictization on the one hand, and to the presence of inclusions (chiefly U and Fe minerals), on the other. The aplite-pegmatite differentiates of Tatride granitoids usually contain the same types of zircon as the granite pegmatites and aplites of the Malé Karpaty Mts. (J. G b e l s k ý, 1979); this allows to assume that they formed in the late aplite-pegmatite stages of the crystallization differentiation of the granitoid intrusion. Their mineralogical character is affected not only by the radiation factor of metamictic process but also by genetic factors (postmagmatic alterations of the rock), which enhance the destructive effect of the radiation factor. Statistical evaluation of morphological parameters (length, width, elongation) of zircons of some of the granitoid samples examined (ZK 47 the ZK 20 the Veľká Fatra; ZK 3 — the Nízke Tatry Mts. ZK 11 — Čierna hora lends support to the opinion that the generations of this mineral are present in the rock.

The set of the granitoids examined shows a definite tendency towards an outstanding increase of the garnet content to the more acid — leucocratic types, and towards the extreme content in some aplite types of granitoid differentiates. These garnets are of almandine-spessartine composition with a prevalence of the almandine component. The distribution of Fe and Mg also displays a slight and systematic zonation and mutual compensation, which follows from their isomorphous substitution, i. e. the mixing of the almandine and spessartite components. The gradual zonation (garnet in the granite of Suchý) is interpreted as a primary phenomenon caused by the changing growth mechanism and character of diffusion, which is affected by the thermal conditions of crystallization. In studying the chemistry of the fundamental types of garnets of almandine-spessartite composition from the Little Carpathian pegmatites (J. G b e l s k ý, 1980) the interpretation of the primary magmatic genesis has been inferred from the systematic changes observed: In the long-term process of garnet crystallization, the differentiation of pegmatite melt was accompanied by gradual systematic changes in the concentration of Mn and Fe, and garnets formed the first showed a marked predominance of the almandine components and a tetragon-trioctahedral habit. In the later stages of differentiation connected with a decrease of Fe content and increasing concentration of Mn, almandine-spessartites crystallized; they had a shape of rhombic dodecahedron and approximately equal portions of the two components.

In the granitoid rocks of the Tatride crystalline complex the almandine-spessartites are genetically placed in stages of primary magmatic crystallization differentiation in case they have a homogeneous composition, fresh appearance and idiomorphic development of the above-mentioned basic crystallographic forms. However, there is a frequent occurrence of strongly "contaminated" inhomogeneous garnets with inclusions of mafic minerals and "weathered" surface. These garnets were probably derived either from the rocks of pre-granitization stage (xenocrysts) or from the rocks assimilated by the intruding magma. This interpretation of their genesis is supported by the presence of associated minerals such as pyroxene, hornblende, andalusite and sillimanite, which are not typical of the granitoids in question (Suchý, Nízke Tatry, Vysoké Tatry, Považský Inovec Mts.). In conjunction with other minerals — andradite (with inclusions of Cr-magnetite) grossular, or almandine-spessartite with a

substantial representation of the grossular component (the Malá Fatra, Vysoké Tatry Mts.), corundum and magnetite (?) nodules constitute a mineral association that indicates contamination of rocks, and thus of crystallization medium during magmatic differentiation. The major part of minerals of the above association is genetically atypical of the granitoids in general and probably not very plausible in the leucocratic and aplite-pegmatite differentiations of the granitoid intrusions. To interpret it in terms of their marginal position in the plutons is less probable with respect to the presence of hornblende, pyroxene and/or magnetic nodules in typical dyke pegmatites (J. Veselský — J. Gbelský, 1978), where granite is the only country rock. It seems that the source of contamination of the pegmatites, aplites and leucocratic and aplite-pegmatite differentiates is to be sought in deeper zones where the anatexis processes take place.

The association of accessory heavy minerals reveals the role of pneumatolytic-hydrothermal stages in the development of the West Carpathian granitoids. In addition to the minerals cassiterite, topaz, molybdenite, fluorite, tourmaline, arsenopyrite and rutile — nigrine that are mentioned above, the association of minerals of hydrothermal origin comprises a part of pyrites, carbonates (calcite, siderite), part of galena and hematite, barite and cinnabar. Galena and pyrite have also been established as secondary products after arsenopyrite, hematite after magnetite and siderite, limonite-goethite after magnetite and pyrite, leucosiderite dominantly after ilmenite and less frequently after sphene, and minerals of the epidote-zoisite group are secondary products of the post-magmatic alteration of feldspars and biotite.

The study of the set of the West Carpathian rock samples has shown that the Veporide granitoids are characterized by the following association of accessory minerals (I. Broška, 1979):

EPIDOTE—ZOISITE—APATITE—ALLANITE—SPHENE—ZIRCON—
MONAZITE—MAGNETITE—ILMENITE—PYRITE

The composition of this association is broadly uniform within the whole area studied but the quantitative representation of individual minerals varies considerably. From the investigation of the Veporide granitoids it is evident that the hydrothermal processes took part in the general development of rocks. It is, however, impossible to decide whether the hydrothermal solutions derived from the intruding magma or originated under the conditions of regional metamorphism in the deeper zones of the earth's crust. The possibility of hydrotectonic alterations caused by the motion and action of magma on the mineralized sediments of higher stratigraphic complexes is also acceptable. The superimposed metamorphic processes might give rise to minerals such as corundum, andalusite and rutile (biotite granodiorite, ZK 58). The cinnabar (leucocratic granite ZK 69) is considered to be a product of late Variscan or Alpine neomineralization, because it can occur only in tectonically rejuvenated areas, where it has not yet been removed from the site of crystallization by denudation, i. e. from shallow nearsurface parts of the rock. From this it follows that the origin of other hydrothermal minerals (pyrite, galena, sphalerite, siderite, arsenopyrite, barite and limonite-goethite) can also be associated with the late Variscan or Alpine tectonic cycle. A large part of minerals of the

epidote-zoisite group is actually a saussurite aggregate. Saussuritization and sericitization of plagioclases have not been established in the sample of the Muráň granite-gneiss (ZK 6), which probably did not undergo these processes. The granitoids of the Veporide crystalline complex also show contamination by rocks of the mantle (leucogranite, ZK 69), indicated by the presence of hornblende and garnet (biotite granodiorite, ZK 72), by 80 % of apatite with intensely developed pleochronic nuclei, and abundant inhomogeneous zircon. The appreciably increased garnet amounts and the presence of hornblende (leucogranite, ZK 69) probably represent assimilation of the material of the sedimentary mantle. It can be admitted, however, that the material needed for the formation of garnets was provided by sericitization of plagioclases (biotite granite, ZK 2; leucogranodiorite, ZK 67) with regard to their abundant occurrence linked just with minerals altered in this way. The established association of accessory minerals makes it possible to assess the role of the magmatic, post-magmatic, pneumatolytic-hydrothermal, metasomatic and metamorphic stages in the development of the granitoids of the Veporide crystalline complex.

The Gemeride granites, whose set of samples examined may be ranged to leucocratic granites — alaskites to greisenized granites, display some peculiarities in the occurrence of accessory minerals (J. Veselský, 1978). Compared with the granitoids of the Tatro-Veporide region, they are distinguished by a high frequency not only of such minerals as fluorite, cassiterite, arsenopyrite, wolframite and sphalerite, but also of tourmaline. The greisenized types have a lower frequency of epidote-zoisite, sphene and ilmenite but a strikingly increased frequency and contents of tourmaline (attaining more than 3500 g/t) and above all of cassiterite, scheelite, topaz and wolframite.

The qualitative and quantitative study of accessory-mineral associations in the selected samples of the West Carpathian granitoids is at present in the final stage; it only remains to complement the results from the crystalline regions of the Malé Karpaty, Nizke Tatry Mts., Veporides and Gemerides.

On the basis of the results thus far achieved the following generalization of characteristic associations and mineralogical features can be submitted for two fundamental petrographical groups of the granitoid rocks (J. Veselský — J. Gbelský — I. Broska, 1981).

The biotite granitoids to tonalites are distinguished by a quantitatively richer representation of accessory minerals (in g/t of rock), which is reflected in relatively high index numbers expressing the weigh percentage of accessories in a rock. For these rock types the index numbers are also increased because of high contents of minerals of the epidote-zoisite group. Relatively high contents, however, have also been established for zircon, apatite, sphene, allanite, magnetite, pyrite, and for secondary limonite-goethite and leucoxene. Zircons usually lack all signs of metamictization and show a relatively homogeneous composition. Apatites are fairly often of smoky colouration and contain pleochroic nuclei, which indicates hybridization of the medium of crystallization. The high content of minerals of the epidote-zoisite group is usually accompanied with an increased content of sphene, magnetite and occasionally of ilmenite. High contents of these minerals in biotite-rich rocks are invariably associated with its alterations, as they form e. g. by chloritization of biotite at the expense of segregated Fe and Ti.

In the leucocratic to two-mica granitoids, the above-mentioned minerals decrease in amount or they are not present at all, whilst other minerals appear. These are typical of this group of granitoids and involve monazite, xenotime and garnet. The last one often occurs in a strikingly increased amount, and is usually of almandine-spessartite composition; part of it is genetically ranged to the primary magmatic minerals, originating in succession of biotite. Among the rare minerals are rutile — nigrine, anatase, tourmaline, arsenopyrite, molybdenite and topaz. A particular phenomenon is an almost systematic contamination with minerals that are not regarded as their primary component, such as garnets with a higher grossular component, occasionally with andradite component and inclusions of Cr-magnetite, andalusite, sillimanite, pyroxenes, spinels, hornblende, etc. These minerals may have derived from the rocks of the pre-granitization stage or be components of the rock material assimilated by the intruding magma. Zircons in samples of leucocratic granitoids bear signs of metamictization, and in the aplite-pegmatite differentiates they are represented by destructed metamict cyrtolites with an increased Hf content. In addition to zircon showing traces of metamictization, the late magmatic concentration of radioactive elements is manifested by the crusts of decay products on the surface of monazite and xenotime crystals.

The genetic heterogeneity of the associations of accessory minerals provide evidence of the complicated development history of the West Carpathian granitoid rocks. Some of the accessory minerals are relatively often present in several generations (zircon, apatite, monazite, allanite, garnet, pyrite, magnetite, etc.). All the data obtained so far by the study of accessory minerals indicate not only changes in the chemical and thermodynamic characters of the crystallization medium during primary magmatic differentiation, but also the participation of several geological processes in the overall history of the granitoid rocks of the West Carpathian crystalline complex.

Translated by H. Zárubová
Review by D. HOVORKA

Manuscript received April 20, 1982

Plate 1

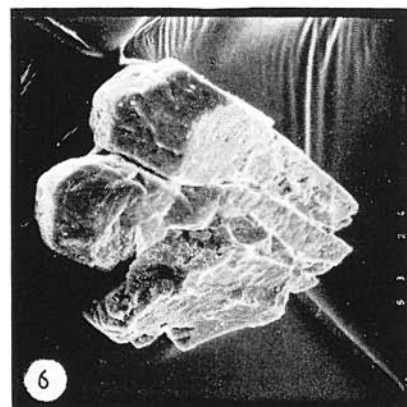
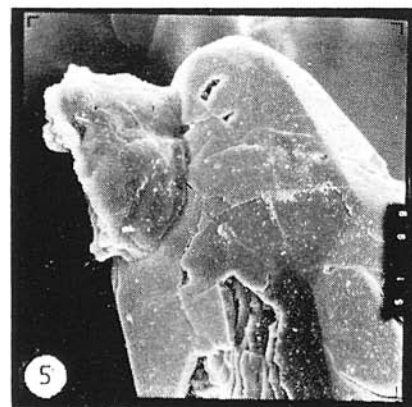
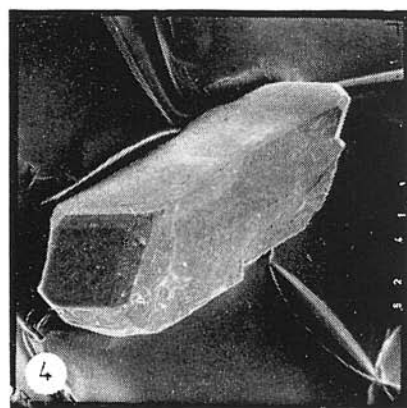
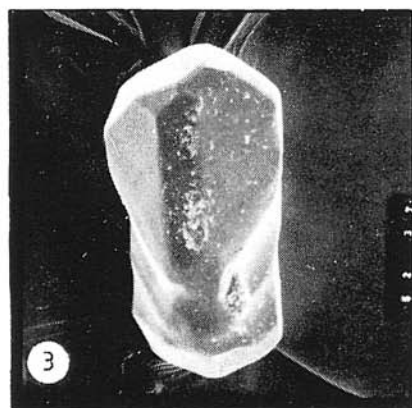
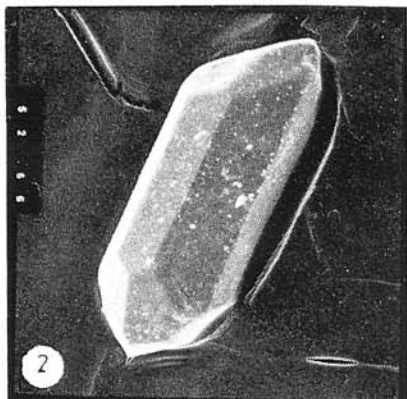
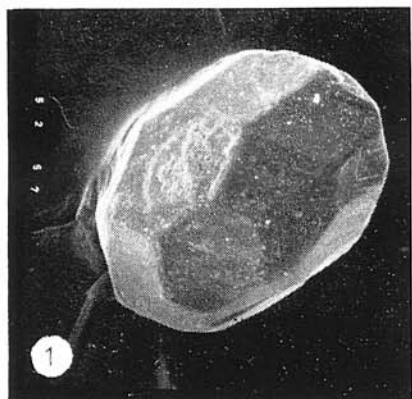


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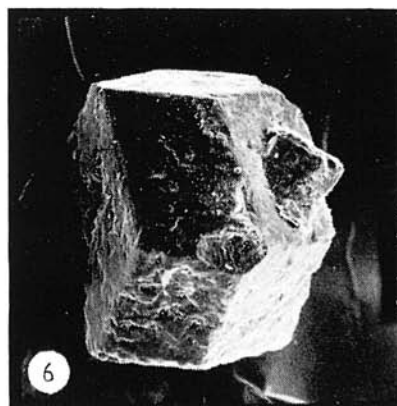
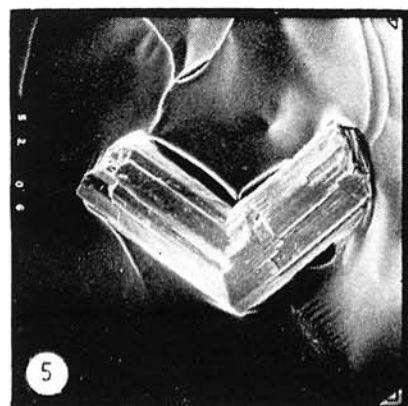
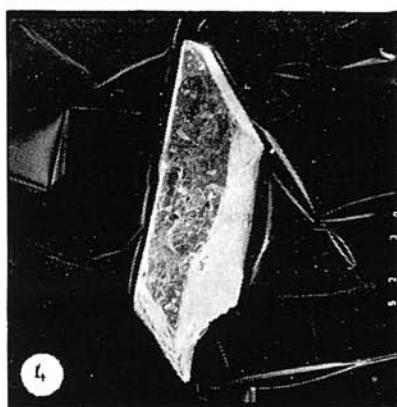
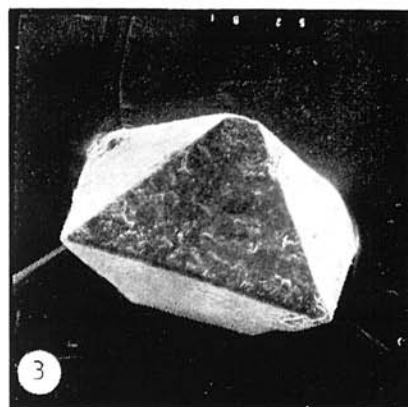
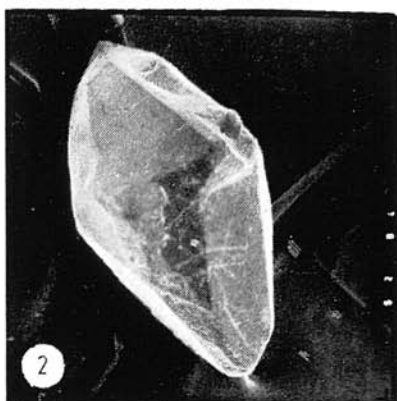
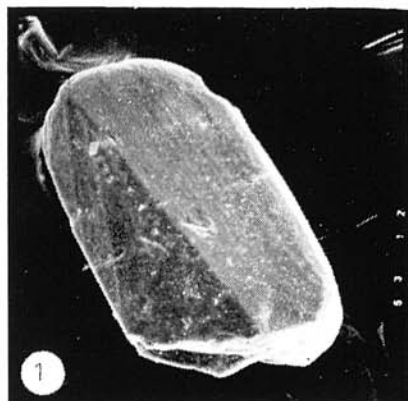


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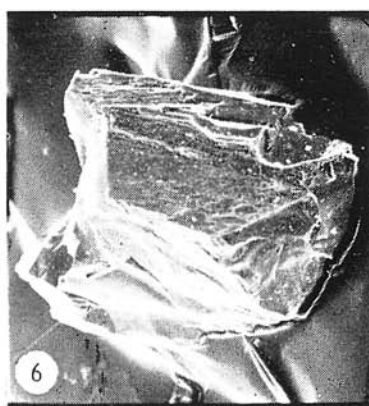
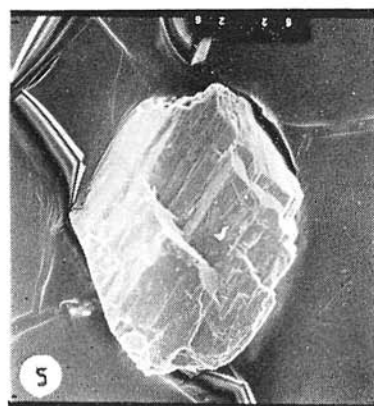
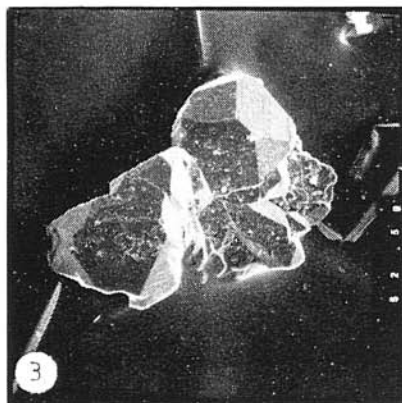
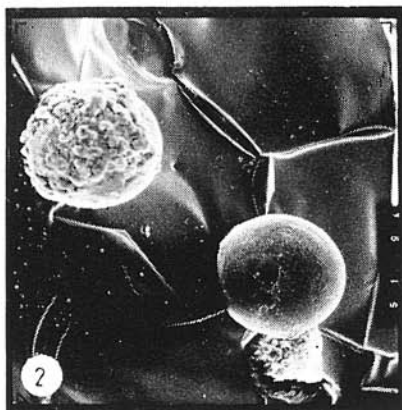
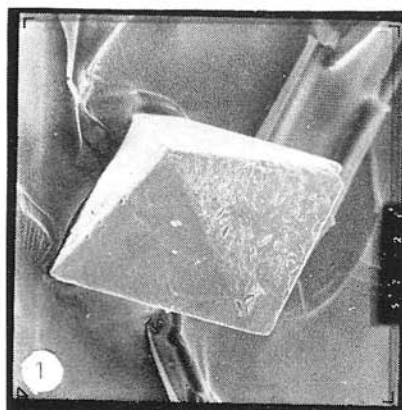


Plate 1

Zircons from granitoid rocks of West Carpathians

Fig. 1. Čierna hora Mts., ZK 11, SEM, x 300.

Fig. 2. Čierna hora Mts., ZK 12, SEM, x 340.

Fig. 3, 4. Nízke Tatry Mts., ZK 24, SEM, x 280, x 300.

Fig. 5. Branisko Mts., ZK 55, SEM, x 550.

Fig. 6. Strážovské vrchy Mts., ZK 59, SEM, x 450.

Photo: K. Šebor, M. Švec

Plate 2

Fig. 1. Apatite from ZK 38, Malá Fatra Mts., SEM, x 500.

Fig. 2. Monazite from ZK 3, Nízke Tatry Mts., SEM, x 240.

Fig. 3. Xenotime from ZK 3, Nízke Tatry Mts., SEM, x 360.

Fig. 4. Sphene from ZK 1, Tribeč Mts., SEM, x 100.

Fig. 5. Rutile from ZK 41, Tribeč Mts., SEM, x 200.

Fig. 6. Garnet from ZK 3, Nízke Tatry Mts., SEM, 180 x.

Photo: K. Šebor, M. Švec

Plate 3

Fig. 1. Magnetite from ZK 47, Vysoké Tatry Mts., SEM, x 320.

Fig. 2. Magnetic modules from ZK 55, Branisko Mts., SEM, x 200.

Fig. 3. Crystals of pyrite from ZK 11, Čierna hora Mts., SEM, x 260.

Fig. 4. Limonite-goethite from ZK 38, Malá Fatra Mts., SEM, x 1500.

Fig. 5. Hornblende from ZK 47, Vysoké Tatry Mts., SEM, x 220.

Fig. 6. Allanite from ZK 38, Malá Fatra Mts., SEM, x 220.

Photo: K. Šebor, M. Švec