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BOHUSLAV CAMBEL* — MILOSLAV KHUN**

GEOCHEMICAL CHARACTERISTICS OF BLACK SHALES FROM THE ORE-BEARING COMPLEX OF STRATA OF THE MALÉ KARPATY MTS.

(Figs. 31, Tabs. 46)

A b s t r a c t: This study consists of five parts. The first part deals with the geology of the Malé Karpaty Mts. with special regard to the development of shale complexes, their metamorphism, the facies, stratigraphic and petrographical conditions, and informs about the distribution of ore deposits in the crystalline complex.

The second part is directed to the investigation methods applied, surveys the present state of knowledge of black shales, based on the world literature, and the opinions on their genesis. It discusses the chemistry of the Malé Karpaty slates and schists, which were divided into sets on the basis of regional-geological and petrographic-lithological criteria. The metamorphic grade and effects of other alterations are taken into consideration. The position of the slate complex either in or outside the ore-bearing zones is an important dividing principle. Particular attention is devoted to black and dark slates and their geochemical study in relation to the intensity of their pyrite mineralization. Migration of microelements in geological processes and their correlation is dealt with.

The subject of the third part is the study of elements of the polymetallic group and of development of antimonite deposits. The authors point out that Sb-deposits were produced as a result of Sb migration after the granite intrusion, when the Sb component had been mobilized from dark shales, in which Sb was primarily present in higher amounts. The knowledge of the geochemistry of ores and mineralized rocks is summarized and the facts clearing up the genesis of antimonite deposits are pointed out.

The fourth part of the paper concerns the samples that were examined not only by spectral and atomic absorption analyses but also by neutron-activation analysis. In this way there were obtain data on the contents of some rare earth elements (La, Ce, Sm, Eu, Tb, Yb, Lu), of elements that were not determined by other analyses (REE, As, Ta, Hf, W, Ag), and part of elements from samples of the Malé Karpaty crystalline schists, which were analysed by other methods (Au, Sb, Sc, Ga, Rb, Cs, Zn). The results obtained by different analytical methods are compared, and the evaluation of REE contents, the first from the West Carpathian sediments, is submitted. Unfortunately, not all elements of rare earths have been analysed, and part of the results is not of satisfactory quality. Therefore, a complementary geochemical study of these elements has to be carried out in the near future.

The fifth part is virtually a catalogue of chemical analyses of rocks. The numerical symbols given in the catalogue denote to which populations the rock was assigned in statistical and geochemical evaluation. The numerous tables of original and taken-over data from the literature form the basic material for geological-geochemical, petrological and metallogenetic interpretations. The authors are well aware that such abundant documentary material cannot be regarded as satisfactorili evaluated within one publication of limited page number and that it is to be appraised to a greater detail.

* Acad. B. C a m b e l, Geological Institute of the Slovak Academy of Sciences, Dúbravská cesta 9, 814 73 Bratislava.

** RNDr. M. K h u n, Department of Geochemistry and Mineralogy, Faculty of Natural Sciences of Comenius University, Paulínyho 1, 811 02 Bratislava.

Р е з ю м е: Предлагаемая работа состоит из пяти частей. Первая часть объясняет геологическую обстановку Малых Карпат именно с точки зрения развития сланцевых комплексов, их метаморфоза, фациальных стратиграфических и петрографических условий, и дает информацию о распределении рудных месторождений в кристаллинике.

Вторая часть работы направлена на методы исследования примененые авторами, дает представление о современном состоянии в исследовании черных сланцев на основании изучения мировой литературы, и информирует о взглядах на их происхождение. Подает обзор о химическом составе сланцев Малых Карпат, которые распределены в комплекты по регионально-геологическим и петрографическо-литологическим критериям. Учитывается степень метаморфоза и влияние других изменений. Важным принципом расчленения является критерий, относится ли комплекс сланцев к группе пород из продуктивных рудоносных зон, или находятся ли они вне этих зон. Особое внимание уделяется черным и темным сланцам и их геохимическому изучению в зависимости от интенсивности их пиритового оруденения. Исследована миграция микроэлементов во время геологических процессов и их взаимные корредяционные отношения.

В третьей части работы внимание уделяется элементам полиметаллической группы и причинам образования аккумуляций месторождений антимонита. Авторы подчеркивают, что Sb — месторождения возникли как продукт миграции Sb после гранитовой интрузии, когда был Sb-компонент мобилизирован из среды темных сланцев, которые первоначально содержали сурьму в высшем количестве. В работе находится совокупность знаний о геохимии руд и орудененых пород и обращено внимание на факты объясняющие происхождение месторождений антимонита.

Четвертая часть работы касается проб, которые кроме спектрального анализа и анализа атомной абсорпции подверглись и нейтронно-активационному анализу. Таким образом был получен обзор о содержаниях некоторых элементов редких земель (La, Ce, Sm, Eu, Tb, Yb, Lu) и о содержаниях элементов, которые не были анализированы другими методами (REE, As, Ta, Hf, W, Ag), и часть элементов (Au, Sb, Sc, Ga, Rb, Cs, Zn) в тех же самых пробах кристаллических сланцев Малых Карпат, которые уже подверглись анализу другими методами. В четвертой части сравниваются результаты анализов полученные при помощи разных методов, и излагается оценка содержания REE, которая пока единичная из осадочных пород в области Западных Карпат. Жаль, что не все элементы редких земель анализированы, и часть результатов, что касается качества, неудовлетворительна. Поэтому необходимо будет провести позже дополнительные исследования относительно геохимии элементов приведенных проб.

Пятую часть работы составляет каталог химических анализов пород. В каталоге приведены и цифровые символы обозначающие, в которые комплекты была порода включена во время ее статистической и геохимической оценки. Многочисленные таблицы подлинных и из литературы перенятых аналитических данных составляет весь основной материал для геолого-химических, петрологических и металлогенетических интерпретаций. Само собой разумеется, что эти многочисленные документальные материалы публикаций ограниченные объемом страниц, нельзя еще считать достаточно оценными, и авторы будут к ним еще возвращаться.

I. Geology and metallogeny of the Malé Karpaty Mountains

I.1. Survey of investigations of the Malé Karpaty Crystalline and the aim of the study

The Malé Karpaty Crystalline has long attracted attention of geologists because of its interesting structure and mineral wealth, particularly in the Pe-

zinok—Pernek area. The region was studied, for example, by Kornhuber (1858), Adrian — Paul (1864), Beck and Vetters (1904), Richarz (1908) and Toborffy (1916, 1917—1924). After World War I, the south-western part of the Malé Karpaty Mts. was studied by Koutek — Zoubek (1936). The crystalline complex of this mountain range was the object of many papers of Cambel (see the references). Since 1965 Cambel with his collaborators has published numerous works (incl. monographs). The team investigations, which make possible an integrate study of the problems, are under way and part of the papers are cited in the References.

The exploration of ore deposits in the Malé Karpaty region was conducted in the past by Beyschlag, Krusch and Vogt (1913), Lachmann (1915), Krusch (1916) and Pauk (1937). After World War II, the question of mineralization in the Malé Karpaty region was studied by Cambel — Kupčo (1952, a monograph), Cambel — Böhmer (1955), Cambel (1959), Cambel — Jarkovský (1967, 1969, 1979), Kantor (1974 a, b, c), Polák (1955, 1974), Polák — Hanas (1981), Polák — Rak (1979), Khun (1977, 1980), and others.

Recently, Cambel with his collaborators (RNDr. M. Khun, Ing. V. Streško, CSc., RNDr. Mičuda, RNDr. V. Kátlovský, CSc.) have published a number of articles concerning the geochemistry of ore-bearing zones and ores involved, and the geochemistry of some principal rock types of the Malé Karpaty Crystalline (coauthors: Doc. RNDr. J. Veselský, CSc., RNDr. M. Khun, RNDr. V. Vilinovič, RNDr. J. Spišiak, CSc.). The publications of these authors are listed in the References, and many data and results are included in this work.

The aim of this publication is to inform on the present state of knowledge of the geochemistry of the rocks forming the ore-producing zones, of ores and other rock types. The results achieved contribute to the solution of genetic problems of the pyrite and antimonite mineralization in the Malé Karpaty Mts.

The paper endeavours to make accessible and catalogue especially the analytical-geochemical records, which are the primary documentary material for relevant petrological, metallogenic and minerogenetic interpretations and deductions.

It aims at assessing the clarke (background) contents of elements important lithologically as well as those which are significant from the view-point of metallogenic processes and processes leading to accumulation or dissemination of ores. It also stresses the need of mathematical treatment of geochemical data for compiling the sets (populations) arranged according to characters of interpretative significance.

In order to elucidate important petrogenetic and metallogenic processes, various geochemical relations between element contents and correlations of more complicated ratios are applied.

I.2. Geological setting of the Malé Karpaty Crystalline. Division of the crystalline complex

In the Core mountain range of Malé Karpaty the crystalline rocks build up the predominant part of the mountains, mainly its central part and southern

slopes. The complex extends from Horné Orešany on the north-eastern side of the mountain range to Bratislava and across the Danube valley south-westwards into the Hainburg and Hundesheimer Hills.

The principal member of the Malé Karpaty Crystalline are the Variscan late orogenic granitoids which make up more than two thirds of the crystalline complex.

The granitoid rocks form two separate massifs — the Bratislava massif and the Modra massif, which are separated by a zone of Pezinok—Pernek crystalline schists, 4 to 8 km broad. Many granitoid occurrences crop out at the surface of this zone. In addition to this largest schist zone of the Malé Karpaty, a more or less continuous schist belt rims the Bratislava granitoid massif in the NE, between Záhorská Bystrica and Pernek. Another continuous schist complex occurs in the SE between Dolany and Horné Orešany. The slate complex of the Harmónia Group spreads chiefly between the Hrubá dolina, Časta and Dolany. Numerous minor occurrences and blocks are found within the whole complex of granitoid rocks as relics of the mantle.

The principal rocks of the Malé Karpaty schistose crystalline complex are biotite phyllites, biotite-garnet micaschist-gneisses and biotite-garnet gneisses with staurolite or muscovite and sillimanite. Chlorite-sericite phyllites without biotite, representing the low-grade metamorphosed rocks of the greenschist facies, are scarce. In general, the sericite-chlorite phyllites were produced by diaphthoresis, with occurred during the Alpine tectonic reworking of biotite shales. The crystalline schists also comprise various types of amphibole-bearing rock, which are metamorphites of diabase or basalt-tholeiitic rocks and their pyroclastics. Black slates, which even at higher-grade metamorphism show a low recrystallization degree, are frequent. In the Pezinok—Pernek crystalline area the black slates are a componental part of ore-bearing zones with accumulations of pyrite and occasional antimonite deposits.

I 3. The Harmónia Group

The slates between Modra and Časta are defined as a separate facies unit — the Harmónia Group of younger stratigraphic age (Devonian to Lower Carboniferous). It is composed of predominant clayey-siliceous and bituminous slates with a varying portion of carbonate and metabasite basaltoids.

The slates of the Harmónia Group differ from other Malé Karpaty schists in the following features:

1. Pelitic-psammitic pre-metamorphic composition: fine layers of psammitic detritus alternate with pelitic layers of hair-like or greater thickness, which contain strongly carbonatized organic matter.

2. An increased content of carbonaceous component (black slates), presence of lens-shaped carbonate layers, and minor volcanic bodies of spongy structure or hypabyssal layers of amphibole-bearing rocks. The volcanites are accompanied by pyroclastics, and intensified volcanism usually falls in the period of carbonate sedimentation.

3. In contrast to the rocks of the crystalline basement of the Malé Karpaty, the Harmónia Group was not so strongly folded during the Variscan orogeny. Granitoid rocks often penetrated between the sedimentary beds and caused their alteration into hornfelsic biotite phyllite or spotted schists with andalusite.

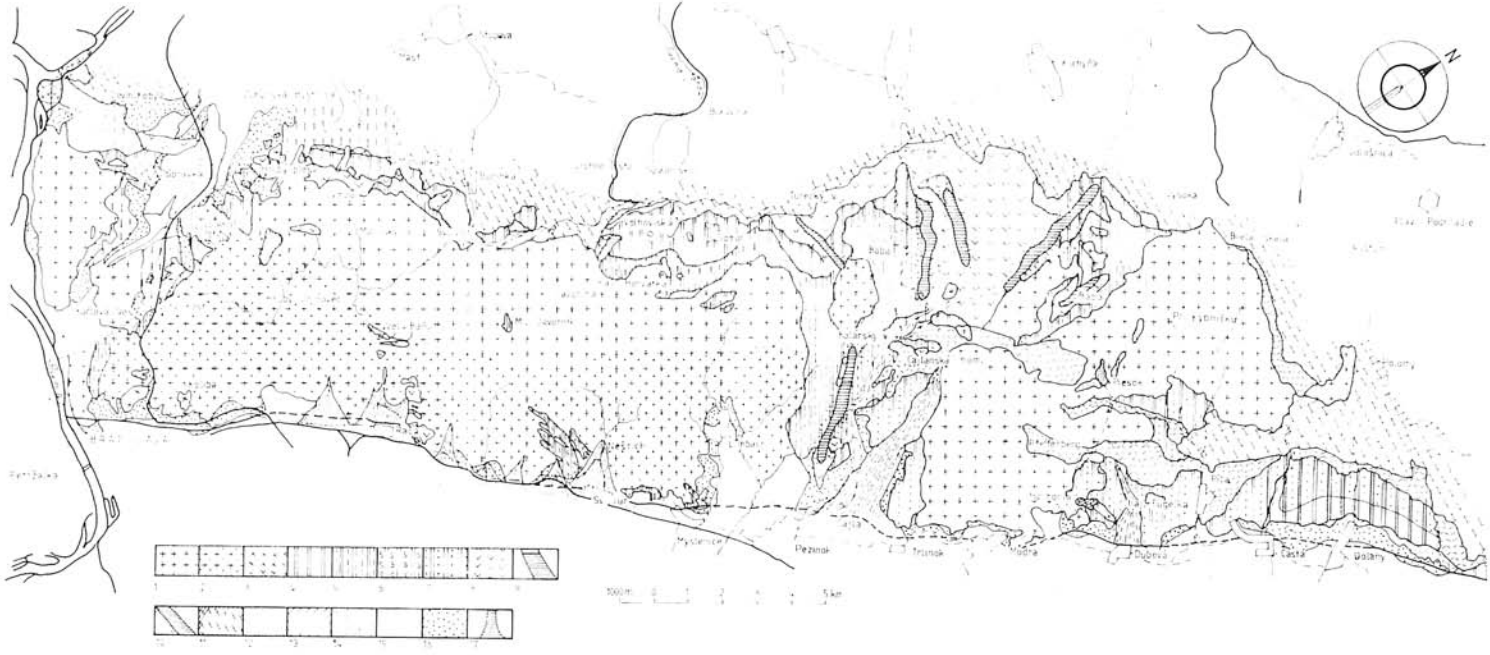


Fig. 1 a. Geological map of the Malé Karpaty crystalline complex

Explanations: 1 — granitoid rocks of the Malé Karpaty Mts.; 2— granitoid rocks with abundant occurrence of pegmatites; 3 — dioritic rocks in granitoids; 4 — phyllites, biotitic phyllites; 5 — biotite-garnet paragneisses; 6 — migmatites; 7 — schists of the Harmónia Group; 8 — amphibolites; 9 — productive ore-bearing zones; 10 — productive zones and black shales in their surroundings; 11 — carbonates of the Harmónia Group; 12 — Lower Triassic quartzites and arcoses; 13 — the rest of Mesozoic rocks undivided; 14 — Neogene rocks undivided; 15 — alluvium; 16 — slope loam; 17 — debris-cones of periglacial origin.

The carbonate-silicate hornfels with diopside, garnet, vesuvian, plagioclases, wollastonite, zoisite and amphiboles formed at the granitoid limestone contact.

I.4. The Pezinok—Pernek crystalline complex

The Pezinok—Pernek crystalline area is the most thoroughly investigated part of the Malé Karpaty; it was studied in detail by B. Cambel and his collaborators, by the workers of the Geologický prieskum, nat. corp. (RNDr. S. Polák, RNDr. R. Žákovský) and Ing. RNDr. J. Kantor, CSc. from the D. Štúr Geological Institute.

The Pezinok—Pernek crystalline area differs from other schistose parts of the Malé Karpaty especially in these features:

1. the occurrence of huge masses of metamorphosed extrusive and intrusive amphibole-bearing rocks with metamorphosed basic tuffs and pyrite-pyrrhotite deposits closely associated with this volcanism;
2. the presence of extensive and numerous layers of black slates with continuous productive zones containing pyrite and antimonite;
3. a particular strike of schistosity, and stratification of crystalline schists, i.e. NW—SE to N—E, which is perpendicular to the direction of the mountain range, whereas in other parts of the Malé Karpaty the schists usually trend more or less parallel to the direction of the mountain range, i.e. NE—SW to NEE—SWW;
4. the exploration of the Sb deposit at Pezinok by boring has revealed that the older complex of the Pezinok—Pernek crystalline unit overlies the younger rocks of the Harmónia Group. As the distance between the deposit and the outcrop of the Harmónia Group is only 300—500 m, it cannot be decided whether a thrust fault is involved or whether the crystalline complex is allochthonous, as is presumed by Maheľ (1980).

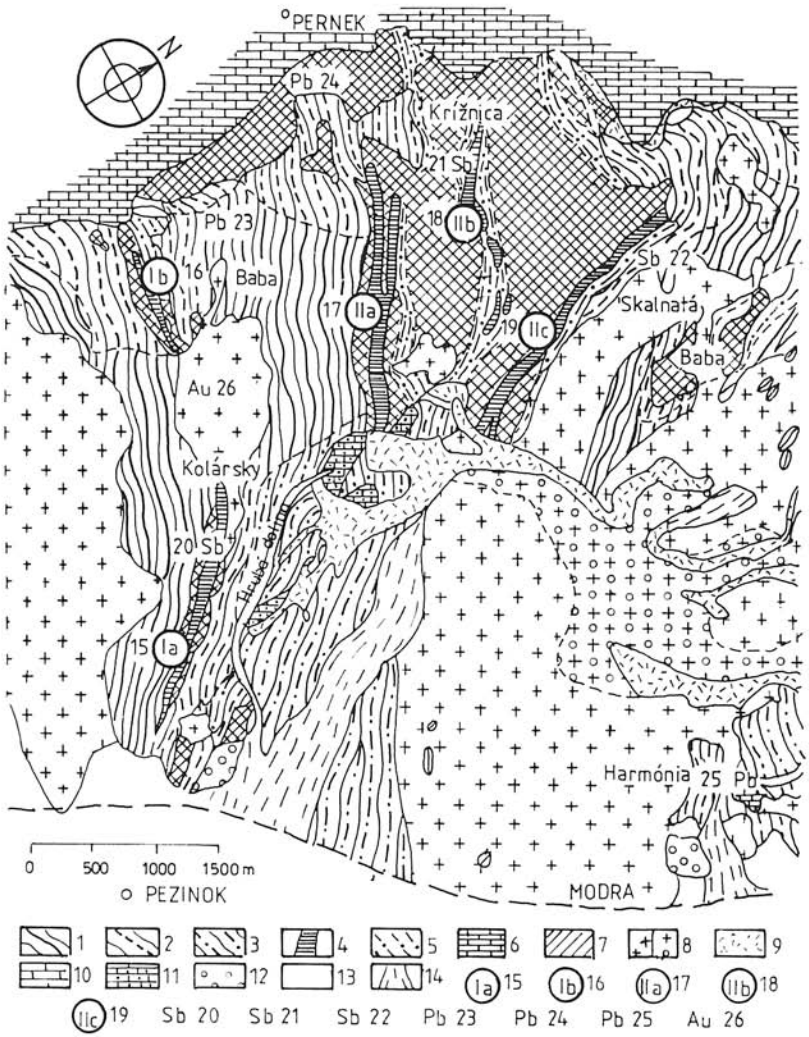
In the area discussed there is a close relationship between the Variscan tectonics and the granitoid intrusion; it is especially on this evidence that we consider the present tectonic style of the Pezinok—Pernek crystalline area to be Variscan for the most part.

Variscan orogeny laid foundation to the stratification and schistosity of the rocks, and the isoclinal structure was disturbed by Alpine disjunctive movements, faulting and overthrusts.

I.5. Ore-bearing zones in the Malé Karpaty Crystalline

The map of the Pezinok—Pernek crystalline area (Fig. 1) shows a certain symmetry in the distribution of argillaceous metamorphic and amphibole-bearing rocks, and of mineralized zones in the central complex of basic volcanics. This symmetry is caused by the genetic evolution of the Pezinok—Pernek zone, by the periodicity of volcanic activity and isoclinal folding of the complex.

Fig. 1 b. General geological map of the Pezinok — Pernek crystalline complex with principal mineral deposits (according to Cambel, 1959).
Explanations: 1 — mica schist and paragneiss (the hachure indicates bedding and schistosity directions); 2 — phyllite; 3 — phyllitic rocks of the Harmónia Group;



4 — the productive ore belt with sulphidic deposits; ;5 — actinolite slate sequence (mainly metamorphosed basic pyroclastics); 6 — limestone in the Harmónia Group; 7 — extrusive and intrusive basic eruptive metamorphosed to amphibolite and amphibolite-bearing rock; 8 — granitoids (1 — 8 — Paleozoic); 9 — quartzite, quartzy arcose, Lower Triassic; 10 — Mesozoic rocks undivided; 11 — light limestone of the Hrubá dolina valley, Middle Triassic (?) (9 — 11 — Mesozoic); 12 — gravel, Quarternary; 13 — loam, slope debris and Quarternary rock undivided; 14 — dejection and solifluction cone. Ore-bearing belts: 15 — Pezinok — Kolársky vrch hill; 16 — Turecký vrch hill; 17 — Rýhová — Augustín — Karol belt, 18 — Rybníček — Čertov kopec hill — Križnica belt; 19 — Köberling — Skalnatá — Kuchynská dolina valley. Deposits and occurrences: 20 — Pezinok — Cajla antimony deposit below the Kolársky vrch hill; 21 — the Pernek antimony deposit below Križnica; 22 — the Kuchyňa antimony deposit; 23 — the lead-zinc district below the Baba hill; 24 — the galena-pyrargyrite deposit of the Svätodušná štôlňa adit; 25 — the galena deposit of the Trojičná štôlňa adit; 26 — gold deposit of the Pezinok district.

The symmetric distribution of rock complexes provides the following picture (see Cambel, 1962): The Bratislava and partly also the Modra massifs are bordered by a ca. 1 km broad zone of gneisses, mica-schists and phyllites. At the margin of the Modra massif this zone was eroded for the most part and only isolated relics remained in the granitoid complex.

Beyond the oldest sediments on the SW side of the Pezinok—Pernek crystalline complex extends the lst ore-bearing amphibolite zone (I). It splits into the southern branch, extending between Pezinok and Kolársky vrch hill, and the northern branch between Konské hlavy and Turecký vrch. They are separated by a spur of the granitoid massif near Kolársky vrch, which is known for the occurrence of gold veins.

On the NE side extends an equivalent belt of amphibolites (ca. 4 km E of Kuchyňa) in the area of Tri kopce, Kuchynská Baba and Gajdoš. This zone (I) does not continue towards Pezinok, having been probably eroded away.

A large complex of amphibole-bearing rocks in the centre of the complex of crystalline schists between Rybníček, Pernek and Kuchyňa, presumably represents the younger volcanic period and is divided symmetrically by three zones of mineralization. In the W it is the zone of the ore field of Rýhova štôlňa and Augustín deposit (II a), in the centre the zone of Rybníček—Čertov kopec—Križnica (II b), and in the extreme east the zone of Köberling—Skalnatá —Kuchynská dolina (II c). The complex of younger and metavolcanic derivatives contains the following deposits in zones II a, II b and II c:

Zone II a: Kristina, Nádej, Augustín, Karol

Zone II b: Čmele I, Čmele II, ore district Pernek with sulphidic and antimonite mineralization

Zone II c: Puklišova and Trojičná galleries near the community Kuchyňa, and syngenetic disseminated pyrrhotite ores near Rybníček and Köberling (Pezinok), in high-grade metamorphosed clayey-siliceous rocks; these contain a considerable dispersed amount of pyroclastics without major accumulations of ore minerals.

The submarine basic volcanism in the Pezinok—Pernek crystalline area was of varied and in a certain degree of pulsative character (Cambel, 1959). Volcanic activity was probably concentrated in two principal periods, and during the intervening interval clayey-detrital sediments without any major admixture of volcanic material were deposited (the overlying argillaceous metamorphites). In each of these periods, the phase of large outflows of basic lava (giving rise to underlying amphibolites) was followed by a phase of minor effusions associated with intensive exhalative activity and ash ejections. Sediments dating from this phase represent productive zones with pyrite deposits. Eventually, there occurred again major effusions or concordant intrusions of basic magma, which gave rise to overlying amphibolites.

I.6. Metamorphic processes in the Malé Karpaty region

After a detailed study of metamorphism Cambel (1950, 1952, 1954, 1956) arrived at the following results:

The crystalline schists of the Malé Karpaty are metamorphic derivatives produced by combined metamorphism — low-grade regional (to the greenschist facies) and subsequent periplutonic, deep-contact process associated with the intrusion of granitoid magma. The gradual penetration of magma developed dynamometamorphic conditions, analogous to those of high- and medium-grade metamorphism, which differ from the normal regional metamorphism by the decrease in the spatial extent of metamorphic effect and thus the thickness of metamorphic zones. In the resulting metamorphic aureoles of granitoid intrusions the gneisses were relatively near the intrusion (at about 1000 m) replaced by micaschist-gneisses and biotite phyllites. Farther from the intrusion the effect of magma only produced a slight development of biotite in the low-metamorphosed slates.

Where the magmatic source is active in higher layers of the crystalline schists the contact metamorphism has not a periplutonic character but that of a typical subsurface thermal isochemical alteration.

This is observed locally at the contact of the granitoids of the Modra massif with the Harmónia Group. The products of this metamorphism are hornfelsic phyllites, spotted and knotted schists, various hornfels types and erlans.

I.7. Stratigraphy of the crystalline complex

The opinion on its age differ. Máška — Zoubek — Buday (1961) consider crystalline schists to be of Proterozoic age. Cambel (1962) and Cambel — Čorná (1974) date the Malé Karpaty crystalline rocks as Palaeozoic on account of the finds of Silurian, Devonian and Lower Carboniferous pollen and plant remains. The Devonian—Carboniferous age is ascribed mainly to the Harmónia Group. The Upper Devonian to Lower Carboniferous plant remains have also been described from underlying schists occurring in the higher metamorphosed complex, e.g. at the western boundary of the granitoid massif (near the crematorium Lamač—Bratislava). Silurian flora has been identified in gneisses near Limbach (Slnečné údolie valley). The Variscan metamorphic recrystallization of schists has been proved by numerous K/Ar analyses made by Bagdasarjan and Gukasjan (Cambel — Veselský, 1981). Horný — Chlupáč (in: Máška - Zoubek - Buday, 1961) claimed the Devonian age for the Harmónia Group on crinoid evidence. On the basis of boring results in the area of a quarry in the Častianska dolina valley, Cambel regards the Harmónia Group as the upper art of the Pezinok—Pernek Crystalline, with regard to the fact that in the lower complex intercalations and layers of metapelitic rocks increase in amount, which are characteristic of the Harmónia Group. At many places, however, this lies on the underlying Pezinok—Pernek Crystalline tectonically and in the area of the Pezinok Sb-deposit even beneath it.

I.8. Antimonite mineralization in the Malé Karpaty and its relation to stratiform pyrite deposits

The genesis and interrelationships between the mineralization types in the Pezinok—Pernek crystalline complex have not yet been elucidated satisfacto-

rily despite a long study. The main problem, which attracted attention of geologists already in the past, is a common occurrence of pyrite and antimonite in the Malé Karpaty deposits.

The pyrite ores form compact beds in amphibole-bearing rocks (metatuffs and metatuffites) or in dark schists with carbonaceous admixture. Antimonite forms veinlets, impregnations or enriched zones and nests in various types of crystalline rocks, in particular in tightly folded dark phyllites or in compact pyrite beds. Because of the common occurrence of antimonite and pyrite in the same deposits, they were regarded in the past as products of one genetic process.

Lachmann (1915) and Krusch (1916) presumed an identical source of metallogenesis for the two minerals, but they thought antimonite to be older than pyrite on account of its stronger tectonic disturbance. They considered the pyrite layers with broad zones of disseminated pyrite as a product of metasomatic replacement of rocks by the sulphides, wrich gave rise to so-called "fahlbands", i. e. broad "impregnation" zones. In their opinion, the source of mineralization had been the "porphyroids", which are identifiable as spotted amphibolites in the Pernek area.

During the investigations in 1952—1956 carried out by S. Polák and R. Žákovský on the basis of numerous mining and boring works, it was possible to throw more light on the genesis of the sulphite deposits.

Cambel (1959) demonstrated that the pyrite and antimonite mineralizations were two metallogenic processes separated both in genesis and time. The pyrite deposits belong to the sulphide formation of stratiform syngenetic deposits, the Sb mineralization being epigenetic in relation to pyrite mineralization. Additional evidence for this opinion is given in the papers of Cambel, 1959 and Cambel — Jarkovský, 1967.

After the termination of mining explorations, the geochemical studies of Cambel and Jarkovský (1967, 1969) have proved the synsedimentary (stratiform) origin of iron sulphides, on the basis of uniform contents of nickel and cobalt in separated pyrites and pyrrhotites. It is, namely, the formation of sulphides in marine environment under relatively stable thermodynamic and physico-chemical conditions that could ensure a uniform distribution of nickel and cobalt in pyrite and pyrrhotite in various ore deposits of the Malé Karpaty (see chapter III.). Kantor (in: Cambel - Kantor, 1972) proved sedimentary origin of pyrite accumulations on the basis of isotopic study of sulphur in pyrite and pyrrhotite of the sulphide ores. The increased S^{32} isotope content in iron sulphides provides evidence for the influence of bacterial activity.

An analogous method was used to examine sulphur isotopes in minerals of antimony mineralization and the results have shown that antimonites and other Sb-bearing minerals from the Malé Karpaty region have a wide range of isotopic composition of sulphur (Kantor, 1974 b, 1974 c). The increased S^{32} content has been found chiefly in Fe-bearing minerals (bertierite and gudmundite), which form preferentially where the solutions with Sb penetrated rocks enriched in pyrite or sulphidic ores. On the contrary, sulphur of antimonite with S^{32} S^{34} ratio near to the troilite standard, viz. sulphur of deep plutonic character, has a lower S^{32} content.

The study of sulphur isotopes from the region studied thus indicates that

sulphur in antimony sulphides is in some way contaminated and genetically and isotopically heterogeneous.

Of primary importance for the interpretation of the genesis of mineral deposits are the recent finds of scheelite in the concentrates from alluvial deposits of brooks (K a n t o r, 1974 a). Although there is almost no information available on its primary occurrence, K a n t o r found out that the results of heavy analyses were most favourable where the drainage basin extends to the areas of productive ore-bearing zones. This suggests that the occurrence of scheelite is associated with the earlier stratiform mineralization.

According to M a u c h e r (1965) and M a u c h e r — H ö l l (1968), the find of scheelite in the Malé Karpaty called forth the necessity of re-evaluating the genesis of Sb deposits with respect to the possible presence of stratiform Sb-mineralization in this region. The above authors classed the Sb deposits of the Malé Karpaty with the group of Sb-W-Hg deposits belonging to the "time- and strata-bound" type. They presume that this Lower Palaeozoic formation continues into the area of the Spišsko-gemerské rudohorie Mts.

However, the opinion of M a u c h e r and others of the syngenetic nature of Sb mineralization in the Malé Karpaty and of the primary stratiform character of Sb mineralization has not yet been substantiated, not even by extensive boring works.

But these have shown that the economic accumulations of Sb minerals were formed only at the sites of younger hydrothermal activity and where there were suitable conditions for precipitation of sulphides from hydrothermal waters. Thus, a question has arisen whether Sb had been supplied by deep plutogenic hydrothermal waters or whether it had been brought upwards from sedimentary rocks in which antimonite was dispersed, being transported and concentrated later under hydrothermal and metamorphic conditions.

For these reasons a team of workers from the Department of Geochemistry, Faculty of Sciences of Comenius University, and from the Geological Institute of the Slovak Acad. Sci. in Bratislava, began a comprehensive geochemical investigation of the Malé Karpaty crystalline rock complex, and of the productive zones, in particular. The results of these studies concerning the genesis of the pyrite and antimonite mineralizations and their interrelationships are presented in Chapter III.

I.9. Conclusions of the geochemical study of pyrite and antimonite mineralizations

1. The investigations provided information on the contents of economically significant elements of polymetallic ores in the rocks and ores of the Malé Karpaty Mts. The analytical results were checked against the results given by other methods (SPA,* AAS, INAA) to enable correlation and verify their correctness. Particular attention was paid to the contents of microelements in dark slates of the ore-bearing complex in relation to their contents in dark slates occurring outside these zones. The analyses have shown clearly a geochemical particularity of the rocks of the productive zones and thus also the

* further explanations in Chapter II. 3.

particular conditions of the origin of sediments during the activity of submarine basic volcanism.

2. It has been assessed that there is a negligible amount of gold as in dark slates of productive zones and sulphide ores so in granite-gneiss complexes: thousandths to ten-thousandths $g \cdot t^{-1}$. Disseminated gold in pyrite ores increases in amount by metamorphic accumulation, at the formation of concretionary or vein pyrite in primary pyrite ores, by one order of magnitude (hundredths $g \cdot t^{-1}$); tenths $g \cdot t^{-1}$ of gold are contained in hydrothermal pyrite. Disseminated gold in pyrite or primary ores should therefore be regarded as a genetic indicator similarly as Ni and Cu in pyrites of various genesis.

3. The contents of Sb, Au, Pb, Zn, Cu and Hg were determined in both the light and heavy fractions of ores and mineralized slates. As the contents of Sb, Hg, Pb, Au and partly of Zn increase in the light fraction, the authors assume the presence of these elements in disseminated form in primary dark shales and for the most part also in ores, but without participating in the formation of major sulphide aggregates.

4. It has been proved that the dark slates of the productive zones and the syngenetic sulphide ores are enriched in V, Cu, Ni, Sb and less in Hg, Zn, Pb and Au relative to the dark slates outside these zones. Consequently, it is possible to consider the productive complex to be a primary source of metals, which under favourable tectonic and metallogenetic conditions (metamorphic and hydrothermal processes) may have been accumulated into deposits.

5. The differences between the sulphur isotopes in minerals produced by hydrothermal metallogeny (antimonite and polymetallic mineralizations) and in minerals of sulphide deposits have not been explained unambiguously. Therefore, the share of deep magmatic processes and exogenic processes (sedimentation of rocks) in the formation of sulphides cannot be established with accuracy. It should be admitted that sulphur associated with granitoid plutonism took part in the formation of epigenetic antimonite and polymetallic deposits. The ore accumulations may be of juvenile type or mobilized during granitoid plutonism. The authors attach great metallogenic importance to the processes associated with the intrusion of Variscan granitoids and with periplutonic metamorphism of the schist mantle, as well as to hydrothermal processes active in the regressive (late orogenic and postorogenic) phase of the Variscan magmatic-orogenic cycle.

6. The Th and U contents and Th U ratios are of diagnostic value for the geochemical characterization of dark slates and ores of the mineralized zones, in particular, but also of those present outside these zones, including the slates of the Harmónia Group. This finding may help in identification of the rocks of the mineralized zones and thus also in prospecting.

7. The research has provided evidence for a direct relationship between the uranium content and the proportion of organic matter in the rock (sorption form of U bond) and, inversely, a negative dependence of thorium, which concentrates rather as an isomorphic component of minerals, especially of accessories, being independent of organic carbon.

8. The study of relationships between the changes in element contents and schistose complexes of different metamorphic grades indicated that the contents of Sb, and partly of Cu, Hg and As decrease with the increasing grade of metamorphism. The migration trend permits the ascent of elements into

zones with less extreme metamorphic conditions, where major accumulations may develop under appropriate circumstances.

II. Geochemistry of slates of the Malé Karpaty crystalline complex, especially from the ore-bearing zones

II.1. The scheme of geochemical studies

In this part a survey of the results of geochemical studies of the crystalline rocks will be given. The amphibole-bearing rocks have already been discussed in the papers of Cambel, 1952; Cambel — Kupčo, 1965; Cambel — Kamenický, 1982, and they will not be here dealt, with, although the mineralized zones with ore indications contain a large portion of metabasites and metapyroclastics. After all, the stratiform sulphide formation is genetically associated with the submarine basic tholeiite-basaltoid volcanism.

The most relevant problem in the investigation of the clayey-siliceous metamorphics was the geochemical study of dark (black) slates in the Pezinok—Pernek crystalline complex, which are carriers of mineralization and form part of the productive zones. This sequence also contains rocks of phyllitic or gneissic character with a small amount of organic matter. The aim of our study was to define the different types of slates of the productive zones, black slates in particular, and to correlate them with the rocks outside the zones of mineralization and with the rocks of the Harmónia Group, taking due respects to metamorphic and regional aspects of their occurrence.

Some analytical data, on which our geochemical studies are based, have already been elaborated separately by some members of our working team (prof. RNDr. B. Cambel, DrSc., doc. RNDr. J. Veselský, CSc., RNDr. M. Khun, RNDr. M. Dyda, CSc., RNDr. V. Kátlovský, CSc., and RNDr. J. Miklóš). Chemical analyses were carried out in several institutes in Czechoslovakia and the Soviet Union: the names of analysts are given further in this section.

In treating the results obtained we had to take into consideration that several methods were used for geochemical analyses. For example, silicate analyses of schistose metamorphites from complexes outside the productive zones were made using the classical silicate analysis and X-ray fluorescence method. The principal elements of silicate schist, mainly from the productive zones, were determined by the INAA method. Although using this procedure calcium could not been determined, the authors thought it to be satisfactory with regard to a lithological variability of the productive complex. The INAA method made it possible to determine the contents even of those elements that are not definable by SPA and AAS methods, and is thus appropriate for complementing the results obtained by other chemical procedures. It also provides data on rare earths, which are valuable for petrological considerations. (The TR data are given in Chapter III).*

* The analyses published in this paper were made by the following members of the Geological Institute, Slovak Acad. Sci.: RNDr. J. Medved, CSc. (SPA — lithophile elements); RNDr. V. Kátlovský, CSc. (U, Th, K — γ-spectroscopy); Ing. E. Martiny, CSc. (AAS-alkalies); Ing. E. Walzel (silicate analyses); M. Vondrovic (X-ray fluorescence-silicate analyses).

Some analyses were carried out by the members of the Geological Institute of the Faculty of Sciences, Comenius University: O. Karelová, M. Hakoová, RNDr. Kubová, M. Vančo (SPA — lithophile elements); Ing. V. Streško, CSc., RNDr. I. Mičuda, RNDr. O. Škerenčáková (AAS — Au, Sb, Hg, Pb, Cu, Zn). The INAA analyses were made in the laboratory of Czechoslovak Uranium Industry, Stráž pod Ralskem, analyst Ing. P. Kotas, CSc. (TR, U, Th, Au and Sb). Macroelements Si, Na, Al, Fe and Mg were determined using the INAA method in Geofyzika, nat. corp. Brno, analyst Ing. J. Bartošek, CSc. Additionally, several original and control analyses carried out in the laboratories of IGEM Moscow, IGEM Kiev and in the Geochemical Institute, Irkutsk, were used.

II.2. Sampling methods and preparation of rocks for analyses

The sampling of dark slates in the Malé Karpaty crystalline complex for the purposes of Research Project II-4-6 1 was started in summer 1975. The samples labelled K were taken before this date and were studied by Kleinertová in 1972, 1974. Of earlier date are also samples labelled OH and samples nos. 111—163, which derive from the collections of prof. Cambel.

Samples were taken from all known occurrences of dark slates, in the amounts of about 2 kg, from boring cores and from pit heaps (in this case at several places of the heap), always in such a manner that a representative sample would be obtained. Every sample was documented and the sampling site plotted on the map of sampling localities. A part of every sample was used for thin sections, part of it stored in a depository, and the remainder used for analysis. In the Geological Inst. of Acad. Sci. in Bratislava the sample was first coarse-ground in a jaw breaker and then in a finer roller mill. The crushed material was sieved on a 0.2 mm-mesh screen, and the coarser material was again ground in a roller mill; this was repeated until the screen residue was as small as possible. The material thus obtained was after quartering used for analyses.

In order to obtain heavy and light fractions from mineralized slates 10 samples of rocks and pyrite ore were taken from the productive zones (in amounts of 3—5 kg). After crushing and sieving (as described above), they were divided into heavy and light fractions according to the following scheme:

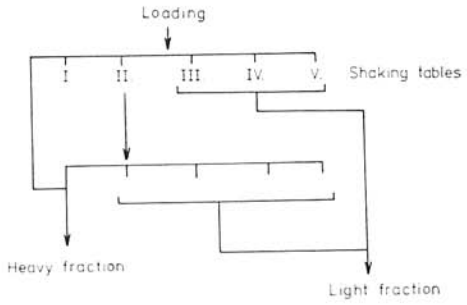


Fig. 2. Scheme of rock separation into light and heavy fractions. I. — V. shaking tables.

II.3. Analyses of black slate samples

All samples examined using the above described procedures were subjected to chemical analyses. The following analyses were carried out:

SPA (spectral analysis):	
elements: B, V, Cu, Ni, Co, Cr, Ba, Sr, Ti, Zr	Spectrochemical Dept. of Geological Inst., Faculty of Sciences, Comenius University in Bratislava
INAA (Instrumental neutron activation analysis):	Geofyzika, nat. corp., Brno
elements: Si, N, Al, Mg, Fe	
INAA — Sb, W, As, Cu, Pb, Zn, Ag, Sc, Ta, Rb, Ga, U, Th, rare earth elements (TR)	Czechoslovak Uranium Ind., central laboratory, Stráž pod Ralskem
AAS — atomic absorption spectroscopy: Au, Sb, Zn, Hg, Pb	Geological Inst., Faculty of Sciences, Comenius University in Bratislava
γ-spectroscopy: Th, U, K	Geological Institute, Slovak Acad. Sci., Bratislava
$C_{org.}$-conductometrically	Geological Survey Prague, branch Brno

The names of analysts are given in Section II.1.

As most of the important results have been obtained by spectrochemical analyses, we will describe here the spectrochemical quantitative analytical method, as used for the black (dark) slates of the Malé Karpaty crystalline complex; it was developed in the Spectrochemical Dept. of the Geol. Inst., Faculty of Sciences, Comenius University.

Working procedure:

A weigh of 0.075 g pulverized sample and 0.175 g of spectrally pure carbon in powder, to which standard elements Pd and Eu were added, was rubbed off for 10 min. in an agate mortar. Two spectral electrodes were filled with this mass. The average composition of the base was (in %):

SiO_2	45.74	MgO	7.79	Fe_2O_3	2.16	K_2O	0.54
TiO_2	2.04	CaO	11.18	FeO	8.12	H_2O^-	0.07
Al_2O_3	17.72	Na_2O	4.20	MnO	0.16	H_2O^+	0.56

Experimental conditions:

Spectrograph: PGS-2 Zeiss Jena; excitation: arc of unidirectional current; source: UBI-1; width of slit: 0.016; projection: 3 f; diaphragm: 3.2; illumination: three-lens lighting; electrodes: active 2.5 × 5 mm SU-103 Elektrokarbon Topoľčany, second electrodes with central projection SU-103; electrode spacing: 4 mm; emulsion WU-3; developing: RO 9 1:20, 20.5 20°C; Exposure: 90 sec.; current intensity: 6A.

Limits of sensitivity ($g \cdot t^{-1}$) and wavelengths of applied analytical lines (μm):

B	30	249.6	Ni	10	441.4
Ti	30	308.8	Co	10	345.3
V	30	318.9	Cr	10	425.4
Cu	3	324.7	Ba	30	455.4
Zr	30	339.2	Sr	30	460.7

II.4. Statistical processing of analytical data and classification of samples

For statistical processing, the data on the contents of elements in the rocks studied had to be arranged and treated, should the required conclusions be obtained. The number of analyses available comprised 190 spectrochemical analyses on 10 trace elements, 159 records of C_{org} contents, 84 INAA analyses for macroelements, 90 INAA analyses for 14 trace elements and 102 data on U and Th contents, determined with γ-spectrometry. For these basic sets the statistical characteristics (arithmetic and geometric means, standard deviation, coefficient of variation), correlation matrices and gradients and x-intercepts for regression lines were computed using a program worked out by RNDr. I. Jedlička on a computer WANG 2200 B, installed in the D. Štúr Geological Inst., Bratislava. To verify the frequency of the contents of micro- and macroelements histograms were compiled, some of which are presented in this paper. The basic sets of analyses were further subdivided according to established criteria and then statistically processed. The sets of macroelements determined by INAA method and sets for spectrochemical analyses of trace elements were subdivided according to the following criteria:

content of organic carbon — less than 0.5 %, 0.5—3 %; above 3 %;
grain-size — fine-grained, medium-grained;
grade of metamorphism — low-, medium- to high-grade (chlorite to amphibolite facies of periplutonic metamorphism):

Fig. 3. Map showing the sampling localities.
The Pezinok — Pernek crystalline complex: 1 — granitoid rocks; 2 — phyllites; 3 — slates of the Harmónia Group; 4 — gneiss; 5 — amphibolites; 6 — limestones of the Harmónia Group; 7— Lower Triassic quartzite; 8 — undifferentiated Mesozoic; 9 — productive ore-bearing zones; 10 — younger formations (Palaeogene, Neogene, Quaternary); 11 — abundant occurrence of black shales in the series of strata.
Bratislava area: 1 — Neogene and younger formations; 2 — Lower Triassic quartzite; 3 — Bratislava granitoid massif; 4 — phyllite to gneiss; 5 — amphibolite and other metabasites; 6 — Mesozoic, undifferentiated (after Cambel — Valach, 1956, modified).

△ sam. 53-56, K 16 ■ sam. 61, 97-100
○ sam. 42-44 □ sam. 82-86 ● Prod. zones
● sam. 29, 45, 49 ▼ sam. 59, 60, 64, 87, 88 ▲ Out of zones
× sam. 90, 91, 105, 108, K13

N
1 2 3 4 5 6
BRATISLAVA
MARIANKA
K3
K18
K19
K17
0 5 10 km
Vysoká
Baba
Kukla
K6
K10
K12
K5
ČASTÁ
MODRÁ
PERNEK
Turecký v.
1000 m 0 1 2 3 4 5 km

content of sulphides — type A = without visible pyrite, type; B = with visible pyrite; type C = pyrite ore;
regional geology — Bratislava massif; Pezinok—Pernek crystalline complex; productive zones — samples of A type, mineralized samples B, C (explanations at Tab. 18); crystalline schists outside these zones; Harmónia Group; underlying schists of the Modra-Orešany area,
stratigraphy — crystalline basement; Harmónia Group (Devonian to Carboniferous) younger formations (Permian—Triassic—Lias),
mineralogy — quartz, more or less discernible; increased amount of carbonates; increased amount of biotite, garnet, feldspars; increased amount of amphibole,
alteration — degree of hydrothermal alteration, mylonitization, or degree of weathering,
schistosity — thinly schistose rocks; massive rocks.

The basic set of analysed samples using the INAA method was divided as follows:

samples of A type from the productive zones;
samples of mineralized rocks and ores B, C (with pyrite) from the productive zones;
samples of rocks outside the productive zones (sample from the Harmónia Group included in the Pezinok—Pernek cryst.);
samples of heavy fractions from mineralized schists and ores.

Discriminant analysis described in papers of Cambel — Khun (1979) and Khun (1980) was used for classifying samples of dark slates of the crystalline complex into groups previously defined, viz. the group of productive zones and the group of rocks from localities outside these zones. For discriminant analysis the mathematical procedure for discrimination between two populations was applied (Sattran — Soukup, 1973; Miller — Kahn, 1962), using a program compiled by Dr. I. Jedlička on a computer WANG 2200 B.

II.5. The present state of investigations of black shales and their genesis

The black shales are a rewarding object of study for geologists, geochemists, economic geologists, mineralogists and petrographers as well. In the past it was obviously because of their rather exotic habit, and at the present time because of their content of trace elements, established thanks to more precise and sensitive methods. The contents of some trace elements are almost of economic values and thus the black shales have become a potential source of mineral raw materials.

Black shales have attracted attention of many authors, both at home and abroad. Among the foreign scientists we should mention, e.g. Trask (1951), Krauskopf (1955), Smirnov (1955), Ronov (1958), Petola (1960, 1968, 1978), Janda-Schroll (1960), Brandenstein-Janda-Schroll (1960), Conant-Swanson (1961), Wedepohl (1964, 1971), Tour-

telot (1964, 1979), Zavjalov et al. (1965), Boyle (1965, 1968), Savul et al. (1965), Vine (1966), Krebs (1969), Vine-Tourtelot (1969, 1970), Vine et al. (1969), Serdjučenko-Potemkin (1969), A. V. Sidorenko — S. A. Sidorenko (1971), Hirst-Kaye (1971), Gucwa (1973), Uspeňskij-Peňkov (1975), Gulson (1976, 1977), Papiu et al. (1975), Poplavko et al. (1978), Konkin et al. (1980), Mitrjajeva-Patalacha (1980) and Vojtkevič et al. (1980).

Of the Czechoslovak authors we should name Flek (1950), Kukal (1961), Varga in Bartalský (1973), Jelínek et al. (1974), Bouška et al. (1975), Vlašimský (1976), Čadková-Mrázek (1980). In recent years an integrated investigation of geochemistry of the black shales in the Malé Karpaty Crystalline has begun and some results have already been published. (Cambel et al., 1975; Cambel-Khun, 1979; Khun, 1980; Cambel-Žukov-Savčenko, 1980; Cambel-Streško-Mičuda, 1981, and Cambel-Kátlovský-Khun, 1981).

II.6. Hypotheses on the genesis of black shales

Opinions on the genesis of black shales differ. According to one theory, they were deposited in an anaerobic environment of stagnant, partly isolated water, poorly aerated and containing H_2S. Some authors presume a shallow-water environment (e.g. shallow parts of Norwegian fjords), others a deep-sea environment (Black Sea). It has also been supposed that the black shales had been deposited in very thick beds over extensive areas, or contrariwise, that they represent a littoral facies or deposits of particular, limited zones of a sea. Hydrological investigations of the Black Sea have shown that black mud is accumulating there at a depth of 1550—2200 m. This led to the opinion that black shales could have originated in similar isolated deep basins, where the basal layers of water are not aerated and are rapidly enriched in sulphur from the accumulated organic matter.

According to other writers, the formation of black shales does not require deep-sea conditions but only a particular, shallow water medium. Ulrich (1911, in Conant, Swanson 1961) assumes that the black graptolite shales of Palaeozoic age developed over extensive areas of open sea, in wide shallow basins, without the necessity of a closed space and stagnant water. The same view was advocated by Twenhofel (in Conant, Swanson 1961); he presumed that the thin beds of the black fissile shales of the Pennsylvanian age were formed "... in extremely shallow water penetrated by sunlight".

Hard (1931 in Conant, Swanson 1961) in describing the Upper Carboniferous black shales in the N.Y. state noted that their close connection with the neighbouring shallow-water sediments excludes other than shallow-water environment for their genesis.

Detailed investigations of sedimentation in the Black Sea and similar basins (Smirnov, 1955) thus far substantiate the opinion on the deposition of black shales in shallow-water environment. They have shown that in the deepest part of the Black Sea, where the stagnancy of water causes its highest contamination with hydrogen sulphide, the sediments contain only a minor amount of organic carbon. The sediments richest in carbon are deposited, on the con-

trary, in shallow water which still contains some oxygen near the estuaries. Accumulation of organic substances in the Black Sea and other similar water bodies is controlled by the character and rate of sedimentation, physical and chemical composition of the sediments and by the biological production of the environment. The stagnant water is not prerequisite (see e.g. the stream-like arrangement of graptolites in some black shales, Bouček, 1932, in Petránek, 1963). A more important factor is an abundance of plankton in semi-isolated basins with inflow of fresh waters, rich in nutrients.

For the Central European Variscicum Krebs (1969) established the following model environments, where black bituminous sediments may have been formed:

1. deep basins in an open sea;
2. closed parts of the basin in an open sea or on shelf
   a) between submarine volcanic ridges,
   b) between growing reefs (e.g. numerous "flinz" sediments of the Rheinisches Schiefergebirge);
3. bases of transgression over flat shelf (e.g. alum shales);
4. flat, limnic-fluvial sedimentary areas.

The schemes proposed by Trask (1951) and Krebs (1969) for the environment of black shales deposition differ. Trask (op. cit.) presumes a stagnant water medium and does not regard its depth as a controlling factor. Krebs (op. cit.) admits for the Central European Variscicum four different types of environment, as given above.

The sedimentological interpretation of the genesis of sulphide black shales may be exemplified by the paper of Cháb (1974) on the Chvaletice deposit. His explanation is based on the theory of Krebs (1969); he admits that a flat shelf existed there at the time of sedimentation and defines the sedimentary medium of the deposit as an unstable shelf whose morphology was affected by volcanism. Volcanic activity persisted throughout the sedimentary interval and presumably strongly influenced the concentration of cations and some anions in sea water.

From the above survey of theories on the genesis of black shales, their non-uniformity and even contradictoriness is apparent. Whether the black shales originated in deep or shallow sea cannot be decided reliably even at the present state of knowledge. It can only be stated that the model of barred basins was and still is accepted by some authors. The recent investigations, however, have shown that black shales had originated during geological history also in very shallow and open sea areas.

Vine and Tourtelot (1970) divided the geological structures appropriate for the genesis and development of typical black shales in the U.S.A. into geosynclines, cratonic basins and shelf.

The fact that the black shales were deposited within a wide range of geological systems indicates that the type of environment of their origin is not of primary importance. More significant were doubtless geological processes occurring in the environment, and such factors as organic production, share of clastic sedimentation and intensity of oxidation which decomposed the organic matter. Where the amount of organic substances was large enough to exhaust oxygen, black shales originated.

According to the most recent hypotheses, the environments in which black

shales can accumulate, are expressed by three models formulated by Didyk et al. (1978). These authors laid great stress on the characteristics of the environment, such as the distribution of O_2 and H_2S in the water column and sediment, and the relationship between organic material and the amount of O_2. In exhausting oxygen the organic matter assists in developing conditions for the accumulation of organic sediments and the production of H_2S.

a) The model of restricted circulation represents the conventional, relatively partial view of the accumulation of organic material in ancient rocks.

A characteristic feature of the model of restricted circulation is the assumption that the content of oxygen in the column of water is restored by circulation and thus accumulation of sediment rich in organic matter may occur even wih a relatively small production of organic matter. Organic material is produced by photosynthesis in the photic zone, mixes with the organic material from the continent (when terrestrial plants exist) and is greatly enriched by chemical and biological processes. At a certain point, however, it is completely consumed by oxidation of the sedimenting material. The exhaustion of O_2 vis not primary but it is caused by a high consumption of it at the decomposition of the organic material. All organic matter is deposited below the zero level of O_2 content, and accumulates at the bottom, where it can be removed only by anaerobic decay. Hydrogen sulphide originating in the bottom sediments may diffuse into higher water layers. The sedimentary environment and sediments are deficient in oxygen.

The model of restricted circulation is represented, for example, by the Black Sea (type of euxinic environment, Goldhaber, 1978) or by the depressions of the fjord type. It can also be applied to basins of tectonic derivation. The structures of fjord type and tectonic basins, however, can not be applied universally as appropriate for the formation of black shales, because of the lack of some morphological features.

An euxinic environment for the origin of black shales in the East Carpathians is also claimed by the Rumanian authors Savul et al. (1965) and Papiu et al. (1975).

b) The model of open sea.

In open sea the content of oxygen may be controlled by the primary circulation, but is also influenced by the amount of organic matter falling from the photic zone through the water column on the sea floor. The minimum of oxygen close below the photic zone is due to the oxidation of organic material. Some more resistant organic matter passing through this interval does not succumb to degradation on its way bottomwards. Also particles sedimenting too rapidly to be completely oxidized, remain intact. Even if a sediment rich in organic matter can accumulate in an environment not deficient in oxygen, several millimetres under its surface it will be "anoxic" on account of the existence of bacterial processes. Consequently, sediments deposited beneath the zone of a high production of carbon may be rich in organic matter and give rise to black shales without the development of oxygen deficiency, as is presumed for a closed basin or cessation of circulation.

c) The model of continental shelf works with the same factors of supply as the other models, but in this case there is not space (water column) enough between the photic zone and the sea floor. Organic material accumulates in the photic zone to a minor extent because it settles more rapidly on the floor.

Oxygen can penetrate up to the surface of sediments thanks o circulation and production of O_2 in the photic zone. Even in this environment the sediments will be deficient in oxygen close under its surface because of the activity of bacteria. The model of continental shelf, similarly as the open-sea model, does not require the presence of H_2S in the water or other conditions analogous to those in the Black Sea.

II.7. Trace elements in black shales; survey of the literature

A wealth of information on trace elements in black shales has been gathered in the numerous papers of foreign, and recently also Czechoslovak authors. In the classical work of Krauskopf (1955) dealing with the sedimentary metallic deposits, the trace elements in black shale complexes are also discussed. In Table 1 compiled from various sources, there are listed average and maximum contents of some elements and mean and maximum values of their enrichment. From this Table K. B Krauskopf inferred that the elements Ag, As?, Cu, Mo, Ni, Au, Pb, V, Zn and Cr are enriched in the black shales, as the average factor of enrichment is four times as high as the background content.

Another important work of earlier date is Wedepohl's paper on cupriferous shales (lithological type of black shales). Besides studying the genesis of them, Wedepohl (1964) presents a comprehensive Table of trace elements contents in different types of black shales. From the stratigraphic data of this Table 2 no relationship between the concentration of trace elements and the age of the rock can be determined. Conspicuous are the contents of V, Cr, Ni, Zn and Mo in the Permian Phosphoria Formation (U.S.A.) and the V, Mo and U contents in the Cambro-Silurian alum shale. All these data relate to unmetamorphosed bituminous black shales. For correlation purposes, analytical data on the metamorphosed black schists from the Precambrian of Finland, according to the author cited, are listed in Table 3. The primary origin of these schists was probably the same as that of clayey shales given in Table 2. The comparison of the two Tables does not show any unusual contents of trace elements in the metamorphosed schists, except for the Cu and Zn contents in Outokumpu schists, for which a secondary supply is postulated. The works of Rösler (Rösler, 1969; Rösler et al., 1971) have also provided important and interesting information.

The topic is further dealt with in the papers of Bain (1960), Barnett (1961), Bitterli (1960), Glagolev (1962), Grant (1964), Katčekov-Flegontova (1964), Geceva — Derjagin (1963), Guljajeva et al. (1965), Curtis (1969) and Cronan (1969).

Among the recent studies on the trace elements in the black shales, the summary work on the geochemistry of black shales by Vine and Tourtelot (1970) is worthy of mentioning. The integrated study of black shales was preceded by investigations of shales in different geological-lithological structures — on the shelf, platforms and in eugeosynclines (Vine, 1966, 1969; Vine-Tourtelot — Keith, 1969; Vine — Tourtelot, 1969). The authors evaluated analyses of trace elements in rocks, made on 779 samples grouped into 20 populations. They introduced the term of "average black shale" and the

Table 1

Average and maximum contents of trace elements in black shales and their average and maximum factors of enrichment

Element	Content		Factor of enrichment	
	average	maximum	average	maximum
Ag	5—50	800	50—500	800
As	75—225 ?	825 ?	15—45	165 ?
Au	0.01—1 ?	7	2—200	1400
Ba	450—700 ?	2400 ?	2—3 ?	10 ?
Be	1 ?	4 ?	0.5 ?	2 ?
Bi	—	100 ?	—	500 ?
Cd	—	300 ?	—	2000 ?
Co	5—50	180	0.2—2	8
Cr	10—500	5000	0.05—2.5	25
Cu	20—300	1000	0.3—4	14
Ga	70 ?	170 ?	5 ?	12 ?
Ge	7 ?	—	1 ?	—
In	—	0.2 ?	—	2 ?
Li	17 ?	660 ?	0.3 ?	10 ?
Mo	10—300	1000	10—300	1000
Nb	0.6 ?	—	0.3 ?	—
Ni	20—300	2400	0.02—4	30
Pb	20—400	700	1.2—25	44
gr. Pt	—	6 ?	—	300 ?
Rb	450 ?	—	1.5 ?	—
REE	25—100	—	0.2—0.7	—
Sb	—	300 ?	—	300 ?
Sc	16 ?	—	3 ?	—
Sn	—	260 ?	—	7 ?
Sr	25—400 ?	2000 ?	0.1—1.3 ?	7 ?
Tl	1 ?	3 ?	2 ?	5 ?
V	50—2000	14000	0.3—13	93
Zn	100—1000	10000	0.8—8	77
Zr	10—20 ?	—	0.05—0.09 ?	—

Taken from Krauskopf (1955). Contents in $g.t^{-1}$. Factor of enrichment = relation of the element content in black shale to its clarke in the earth's crust. Data obtained from a small number of samples denoted by (?).

term "metal-rich black shale", which has higher metal contents than the shale given in Table 1. In Table 4 the average contents of the elements studied in average black shales, as calculated by these authors, are compared with the values given for average clayey shales by other authors.

The topic has recently been dealt with also in the papers of, for example, Haranczyk (1970), Pluman (1971), Burnie et al. (1972), Cosgrove (1973), Dunn (1974), Dančev et al. (1975), Brookins (1976), Papiu et al. (1977), Ashby — Pearson (1978), Gulson — Mizon (1979), Godlevskij et al. (1981) and other.

The contents of trace elements on the Keno Hill deposit in Canada in an ore-bearing shale complex were established by Boyle (1965) and Gleeson-Boyle (1980). For comparison, Table 5 has been compiled in which the average values computed from the data of the above authors are listed.

Table 2

Average contents, range of variation, and methods applied to world localites, arranged

Rock	C %	V	Cr	Co	Ni
Permian clay shale (Phosphoria) Wyoming Davidson, Lakin (1961)	ND	2500 500—7000 SPA	2000 500—5000 SPA	ND	500 150—1500 SPA
Carboniferous, clay shale Montana, Nevada, Utah Davidson, Lakin (1962	ND	2000 1000—3000 SPA	190 75—500 SPA	ND	130 50—200 SPA
Carboniferous, clay shales Kansas, Oklahoma Hyden, Danilchik (1962)	ND	140 70—300 SPA	140 70—300 SPA	15 10—15 SPA	160 150—300 SPA
Carboniferous, Alaunschiefer, Westphalia. Schneiderhöhn (1949)	ND	98 SPA	74	ND	180 SPA
Devonian, clay shale Chattanooga Landis (1962)	4.4 0.3—13.7 Ch.	570 150—3500 SPA	145 15—750 SPA	31 15—150 SPA	170 75—350 SPA
Ordovician, clay shale Thüringen Schneiderhöhn (1949)	ND	5000 SPA	270 SPA	ND	70 SPA
Ordovician — Silurian, clay shales, Thüringen Krejci-Graf (1959)	ND	2600 500—5000 SPA	150 5—500 SPA	90 0—300 SPA	280 10—1000 SPA
Ordovician — Cambrium clay shale Gotland Westergard (1944)	3.5	1070 3—2700 SPA	50 0—95 SPA	27 1—40 SPA	140 30—400 SPA
Cambrian, clay shale Alaunschiefer Gotland Manheim (1962)	17.0 Ch.	470 280—600 SPA	ND	ND	ND
Ordovician — Cambrian clay shales, S. Sweden Landergren, Manheim (1962)	ND	1000 SPA	70 SPA	35 SPA	150 SPA

According to Wedepohl (1964), modified. The authors have *Explanations:* contents of trace elements in $g.t^{-1}$, C in percentages non determined. Quotations are given in Wedepohl.

The Czech authors Jelinek — Pačesová — Bouška (1974) studied the geochemistry of the Proterozoic rocks on the Chvaletice deposit. Average contents of trace elements in sulphidic graphitic phyllites, as determined by these writers are in Table 6.

the determination of selected trace elements various according to stratigraphy

Cu	Zn	As	Mo	Ag	Pb	U
150 100—300 SPA	2800 700—10000 SPA	ND	150 50—500 SPA	7 2—30 SPA	20 10—50 SPA	ND
220 70—700 SPA	1100 200—3000	ND	112 2—300 SPA	4.9 1—15 SPA	21 10—70 SPA	ND
170 70—700 SPA	300 80—700 SPA	ND	23 7—70 SPA	1.7 0.1—3 SPA	25 14—70 SPA	15 10—20 SPA
27 SPA	ND	ND	18 SPA	ND	ND	ND
210 15—750 SPA	160 75—350 SPA	ND	45 7—150 SPA	2.5 0.7—7.5 SPA	33 15—150 SPA	25 10—75 Ch.
110 SPA	60 SPA	ND	200 SPA	ND	ND	ND
ND	ND	ND	50 5—500 SPA	ND	ND	ND
100 56—130 SPA	15 ? 0—15 SPA	32	150 100—250 SPA	ND	36 32—40 SPA	85 15—250
150	330 54—1730 SPA	ND	100 74—133 SPA	1.2 0.9—1.9 SPA	39 33—53 SPA	125 95—150
450 SPA	80 SPA	ND	100 SPA	ND	ND	ND

taken only data concerning the shales of Palaeozoic age
SPA — spectral analyses; Ch — chemical analyses; ND —

Geochemical research of black shales is directed particularly to uranium, in which they are often enriched. S w a n s o n (1961) denotes as uranium-bearing those black shales which contain at least the amount of U = 20 g . t^{-1}. For illustration of the ratios of U, Th, K and organic carbon, their average values (or

Table 3

Average contents, range of variation and methods used for the determination of

Sample	C %	V	Cr	Co
Precambrian black shale, Outokumpu Finland, Peltola (1960)	4.85 2—28.4 Ch.	620 230—1300 Ch.	550 210—3100 SPA	200 100—1000 SPA
Precambrian black shale, Nokia Finland, Marmo (1960)	ND	200 100—300	100	ND
Precambrian black shale, Pohjanmaa Finland, Marmo (1960)	3.4 Ch.	570 80—3500	160 100—600	120 10—700

According to Wedepohl (1964). For explanation see Table 2.

Table 4

Composition of an average black shale (no. 1) and average clayey shales (nos. 2, 3); contents in g . t^{-1}

Element	1	2	3
Ag	1	0.9	0.07
B	50	120	100
Ba	300	800	580
Be	1	7	3
Co	10	12	19
Cr	100	160	90
Cu	70	38	45
Ca	20	40	19
La	30	40	92
Mo	10	0.7	2.6
Ni	50	21	68
Pb	20	20	20
Sc	10	10	13
Sr	200	299	300
V	150	130	130
Y	30	33	26
Zn	300	80	95
Zr	70	200	160

Data taken from Vine — Tourtelot (1970).
1. — Vine — Tourtelot (1970); 2 — Green (1959); 3 — Turekian — Wedepohl (1961).

selected trace elements in the metamorphosed Precambrian black slates

Ni	Cu	Zn	Mo	Ag	Pb	U
400 100—1000 SPA	600 200—700 SPA	400 100—1200 SPA	160 30—470 SPA	2	50 30—100 SPA	51 8—120
570 200—1500	130 50—450	1100 800—2700	70 40—100	0.1	ND	ND
600 100—1500	1100 100—5800	1400 200—6500	93 30—230	2.4 0.1—7.6	40 10—50 SPA	ND

Table 5

Contents of trace elements in the rocks of the Keno Hill deposit, Canada

	I	II	III	IV	V	VI
Cu	2	2	4	4	39	60
Pb	10	2.5	2.5	2.5	13	2.5
Zn	20	20	70	60	69	110
Ni	10	2.5	10	20	26	70
Co	5	2.5	2.5	2.5	2.5	10
As	4	1	1	1	2.5	1
Sb	0.5	0.5	0.5	0.5	1.2	0.5
Mo	0.5	0.5	0.5	0.5	6.2	0.5
W	20	2	2	2	2	2
U	5	1.5	2	2.5	4	2
Sn	7	4	5	5	4	ND
Ag	ND	ND	ND	ND	0.5	ND
Ba	1500	350	750	1200	2533	400

According to Gleeson — Boyle, 1980.
Explanations: contents of trace elements in $g.t^{-1}$; ND — sublimit contents of and Ag; I — granites (4 samples); II — quartzites (95 samples); III — quartz-sericite slates (23 samples); IV — phyllites (76 samples); V — graphitic phyllites (8 samples); VI — greenschists (44 samples).

Table 6

Average contents of trace elements in black graphitic slates of the Chvaletice deposit (contents in $g.t^{-1}$) and Malé Karpaty Mts.

	C (7 samples)	B (5 samples)	B + C (12 samples)	M. K. (190 samples)
Co	43	39	42	13
Cr	224	68	166	92
Cu	110	152	128	91
Ni	66	93	77	114
Pb	167	45	121	
Sn	21	13	18	—
V	283	194	252	358
Zn	54	55	53	184 51

According to Jelínek et al. (1974), modified. C — overlying sulphidic graphitic phyllites; B — underlying sulphidic graphitic phyllites; M. K. — the complete set of the Malé Karpaty slates analysed; numeral in the denominator — number of samples.

only their variation range) and the methods applied to their identification in black shales are given in Table 7.

The modern geochemistry nowadays pays much attention to the study of the elements of rare earths in the rocks. Unfortunately, the data on these elements in black shales are too scarce. The compiled data on the TR elements are presented in Table 8.

In conclusion of this section on the study of black shales, we can state that the main stress has been and will doubtless be laid on the investigation of the contents of trace elements. They are, namely, important for economic reasons as well as from the geological point of view, because they are indicators of the salinity of environment, on the one hand, and on the other, are appropriate for facies analysis (Tourtelot, 1964; Ernst, 1970; Catto et al. 1981) and for solving the stratigraphic problems (Gulson, 1977).

II.8. Localization of the samples analysed and their geochemical composition

The character of slates from the productive zones has been also established in other rock groups of a lesser extent at various places in the crystalline areas (outside the Pezinok—Pernek Group). Of this type are, for example, indications of sulphides near the crematorium and in the wider area of Bratislava—Lamač, in the valley of the Bystrica brook, around the Marianka village (in the large quarry), near the hills Veľká and Malá baňa in the area of Bratislava—Rača, and in the environs of Kuchyňa and Kuchynská Baba in the Modranská dolina. Some slates layers of the Harmónia Group near Dolinkovský vrch have also an increased content of pyrite and sulphides in places of amphibolite oc-

Table 7

Average contents and variation ranges of Th, U, K and C_{org} in various types of black shales; compiled from the literature and from Malé Karpaty Mts.

Localisation of samples	Th	U	K	Th U	C_{org}	No. of samples
Black sediments from Black Sea Manheim, 1961	11 Rm	7 Rm	3.5 Rm	1.5	4.6 Ch.	1
Black shales Mansfield, D. A. Spears (1964)	3.7 — 13.5 Rm	1 — 21 Rm	2.9 — 4.5 Rm	0.6 — 3.7	1.3 — 12.2 Ch.	12
Black shales South Wales, T. W. Bloxam (1964)	12.3 Rm	4.0 Rm	3.2 Rm	3.2	1.2 Ch.	32
Black shales, base Silurian J. Čadek et al (1975)	5.7 Rm	12.8 Rm	1.6 Rm	0.4	2.57 Ch.	38
Black shales from Malé Karpaty Mts, crystalline area Productive zones (ore--bearing)	3.23 Rm	15.15 Rm	1.18 Rm	1.15		62
Outside zones	7.66 Rm	4.27 Rm	2.68 Rm	2.42		40
Harmónia group	9.20 Rm	4.30 Rm	2.79 Rm	2.59		17

Contents of Th and U in $g.t^{-1}$, K and C_{org} in per cent. Rm — determined radiometrically; Ch — determined chemically.

currence. From the above it follows that in the Malé Karpaty region the precipitation of sulphides during re-activated volcanism is a common phenomenon. This fact is likewise apparent from the Ni-Cu correlation graph in Fig. 4, 5 which shows increased contents of pyrite and chalcopyrite not only in the principal productive zones but also in sedimentary rocks of other areas.

The lithofacies and petrographic characteristics of the rocks studied are as follows: The rocks of the underlying schistose sequence and of the Harmónia Group originated by metamorphism of clayey-siliceous sediments, originally of the definitely clastogene character for the most part. The oldest schists, presumably Precambrian, which were deposited in the pre-Variscan geosyncline during the Late Proterozoic to Middle Carboniferous, contain a varying amount of quartz, clay minerals and more or less coarse-grained clasts of crystalline rocks. These rocks were metamorphosed to the greenschist facies during the pre-intrusive phase of the Variscan granitoid magmatism and underwent periplutonic contact metamorphism in the course of the Variscan granitoid plutonism.

Table 8

Compiled data on the contents of REE elements in black shales (g . t^{-1})

	1	2	3	4	5	6	7
La	10.2	17.2	9.6	19.5	12	4.9	20
Ce	22.5	37.8	23.3	36	34	12.2	42
Pr	3.1	3.6	2.9	4.9	—	1.8	6
Nd	14.1	15.6	13.1	20.5	6.9	3.6	16
Sm	3.2	4.1	3.5	3.9	1.7	1.2	5.6
Eu	1.0	1.4	1.1	0.5	0.4	0.5	1.1
Gd	3.2	4.7	3.5	3.9	—	1.2	4.3
Tb	0.5	0.8	0.5	0.5	0.25	0.2	0.6
Dy	2.8	5.8	3.4	2.9	—	—	—
Ho	0.5	1.3	0.6	0.5	—	0.2	0.6
Er	1.4	3.6	1.9	1.6	—	0.5	1.9
Tm	0.2	0.5	0.3	—	0.2	0.1	0.3
Yb	1.5	3.6	1.8	1.4	0.8	0.4	1.8
Lu	0.2	0.6	0.3	0.2	0.1	—	0.3
Y	14.4	30.4	14.1	18.5	—	4.0	18

Explanations: 1, 2 — black shales; 3 — black sulphidic shale, all Kambalda, Australia, Baviston — Taylor (1980); 4 — black graphitic shale, Krivoj Rog, Tugarinov et al. (1973); 5 — black siltstone, Lower Cretaceous, Robertson (1981); 6 — coal, W. Pennsylvania, Schonfield, Haskin (1964); 7 — black shale, Cansas, USA, Haskin — Gehl (1962).

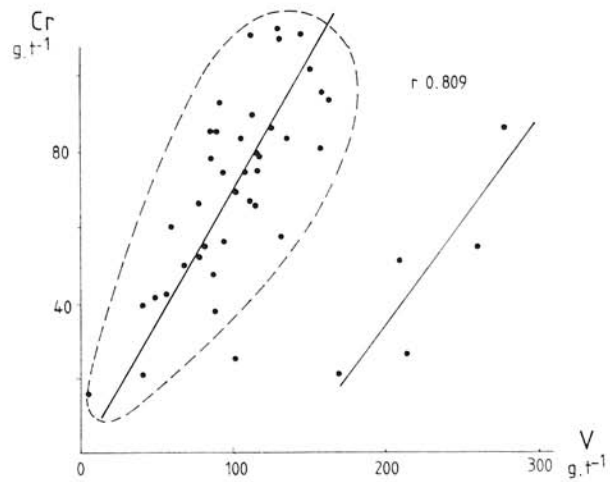


Fig. 4. Correlation graph for Cr V.

The content of basic pyroclastics and a large amount of organic substances and sulphides (mainly pyrite) also influenced the lithofacies development of the sediments. In the Harmónia Group and in the rock complexes of the underlying unit, carbonates occur particularly where there are amphibolites. These components also controlled the character and grade of metamorphic recrystallization and the final composition of the metamorphosed rocks, which in turn governed the content of microelements in the rocks (see graphs 7, 8).

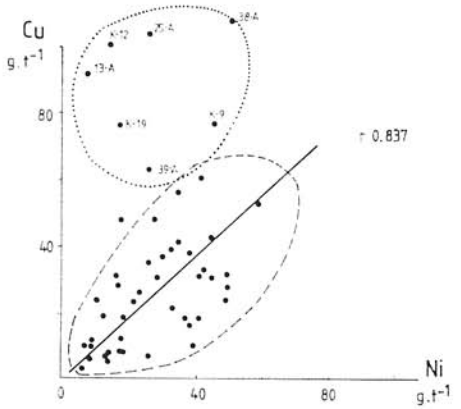


Fig. 5. Correlation graph for Cu/Ni.

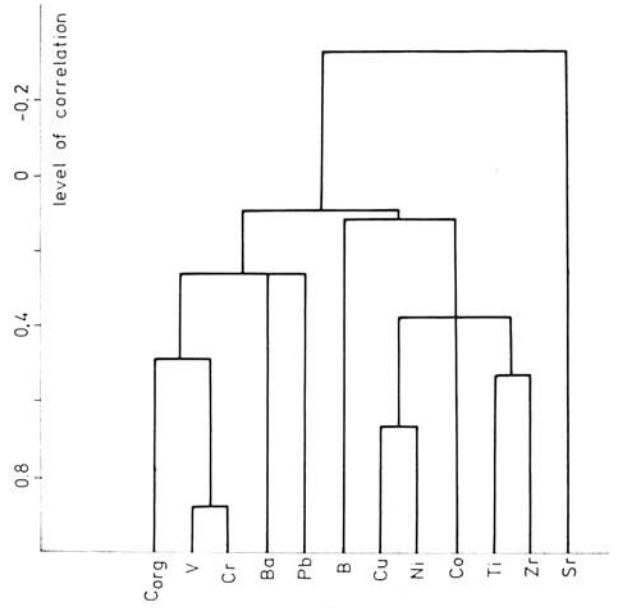


Fig. 6. Dendrogram of trace elements studied in black slates.

The facts mentioned above indicate that the lithological variability and polymetamorphism caused the petrographical heterogeneity of the rocks under study.

Black slates of the productive zones and other rocks containing organic matter outside the ore-bearing zones can be characterized petrographically as me-

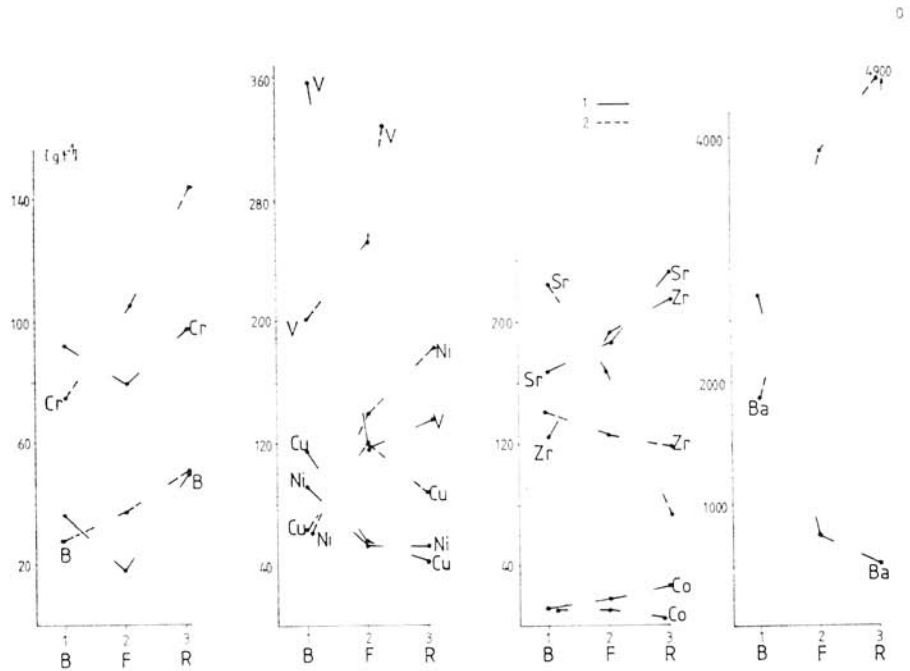


Fig. 7. Average contents of trace elements in black slates, arranged according to the increasing content of organic matter, and in metamorphites of the Malé Karpaty crystalline complex.

Explanations: B — slates; F — phyllites; R — gneiss; solid line no. 1. Content of C_{org}: 1 — less than 0.5 %; 2 — 0.5 to 3 %; 3 — above 3 %; dashed line no. 2.

tamorphosed dark to black clayey-siliceous sediments, showing a low degree of recrystallization and different transitions to sericite-chlorite slates up to phyllites, with initiating development of biotite. With the minor content of organic matter, recrystallization leads gradually to the formation of biotite-garnet phyllites to gneisses with muscovite, staurolite or sillimanite. The slates of the Harmónia Group are altered into hornfelses of different compositions (e.g. calc-silicate), or into spotted schists.

At the presence of pyroclastics, metamorphic rocks of the type of amphibole schists and phyllites originate; they contain different amounts of amphibole and pass into amphibole gneisses to amphibolites.

The presence of a larger amount of pyrite leads to the formation of ores with pyrrhotite (quartz-sulphidic and amphibole-sulphidic ores with high content of organic carbon are without pyrrhotite). The metamorphic rocks of the gneiss

type in the Carpathians have been studied separately; in this paper only a Table of mean analyses is published (Table 32).

The first results of the geochemical investigation of the black slates of the Malé Karpaty crystalline complex were achieved and evaluated as early as in 1977, and they are given in the text of this Section. In 1975 a set of 76 samples

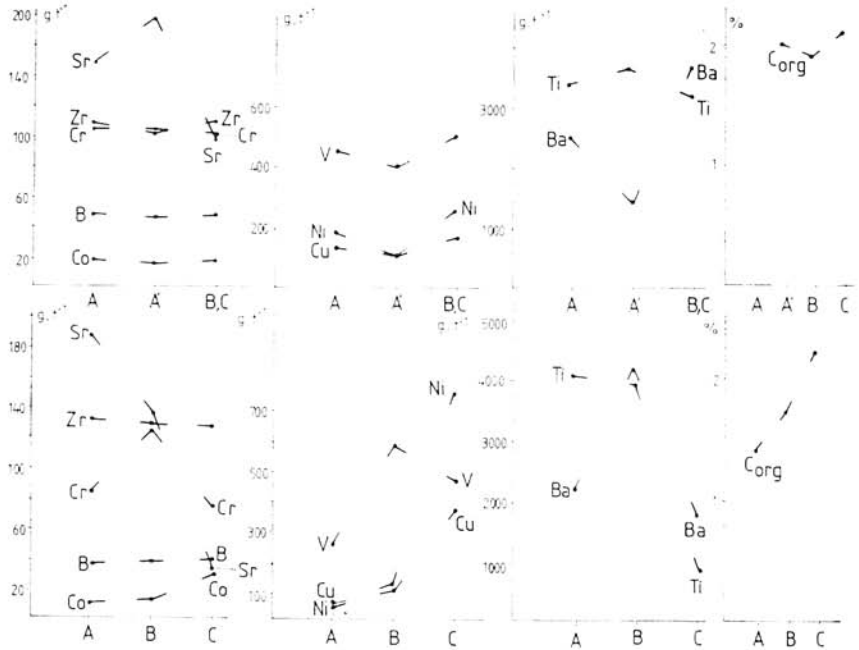


Fig. 8. Average contents of trace elements in the samples of black slates arranged according to the content of sulphides.
Explanations: A — black slates without a visible content of sulphides; B — black slates with megascopically visible content of sulphides; C — sulphide ore. Contents in g.t^{-1}.

was taken and complemented to 102 samples in 1976. At first the study was directed to the rocks as representing a whole, irrespective whether or not they are derived from the ore-bearing zones. The parameters studied were the distribution of selected samples, their correlation, their relation to organic carbon and the mode of bonding of the elements in rocks.

In studying the complemented set of samples, we have taken into consideration whether or not they come from the black slates of the productive ore-bearing zones of the Malé Karpaty crystalline complex. Discrimination analysis using a computer was applied to their distinguishing. Bituminous slates were examined additionally with respect to the content and character of organic substance (C a m b e l — Š i m á n e k — K l e i n e r t o v á, 1975; H a v l í k, 1977).

Table 9

Fundamental statistical parameters of the examined trace elements in black slates of the Malé Karpaty crystalline complex

Element	$\bar{x}$	S	Median	Variation span	Most common content	V (%)
B	44	57	38	0—410	0—20	129
V	386	737	138.5	30—6000	0—150	191
Cu	96	175	38.5	3.6—1350	0—20	182
Ni	114	254	37.5	10—1860	0—40	222
Co	8	9	10	0—65	0—10	112
Cr	113	145	37.5	st—1000	75—90	128
Ba	4956	5193	955	38—10000	10000	104
Sr	175	196	141	st—1950	0—100	112
Ti	4607	2005	4900	410—10000	5000—6000	43
Pb	8	18	10	0—155	0—2	225
Zr	120	55	118.5	30—282	140—160	46

Contents in $g.t^{-1}$. $\bar{x}$ — arithmetic mean; S — standard deviation; V — coefficient of variation in per cent (76 analyses).

Brief conclusions of the investigation of organic matter

The content of organic carbon varies between 0.027 and 13.9 %; the average content in the productive zones is 3.72 % and in rocks outside these zones 2.04 %. The organic matter is in the stage of intensive carbonification, anthracite containing about 2—4 % of other organic substances (bitumens, humins, kerogen) originated from it. The lithofacies character of rocks (fine grain-size of rocks and dispersion of particles) is a decisive factor controlling the quantitative content and qualitative composition of the organic matter.

Dispersed organic substance in rocks altered into strongly carbonified component immediately in the first stages of low-grade regional metamorphism and, therefore, the following metamorphism did not imprint any characteristic features to the organic substances. The only exception to this rule is the increase in the number of n-alkane chains with a higher number of carbons - 20 to 25 (H a v l i k, 1977).

The following elements were examined in the black slates of the Malé Karpaty crystallinne complex: B, V, Cu, Ni, Co, Cr, Ba, Sr, Ti, Pb, Sn, Ga and Zr. They have been divided into four groups on the basis of their occurrence and content:

1. elements that occur in black slates in a higher concentration and that have been identified in all samples: Ti, Ba, (V);

2. elements currently present in black slates in an amount of up to 200 $g.t^{-1}$, and established in all samples: V, Zr (Cr, Sr, Ba);

Table 10

Correlation matrix of trace elements in black slates of the Malé Karpaty crystalline complex

	B	V	Cr	Ba	Pb	Cu	Ni	Co	Sr	Ti	Zr
B	1.000										
V	0.013	0.999									
Cr	—0.045	0.809	1.000								
Ba	0.106	0.300	0.183	0.999							
Pb	—0.021	0.117	0.000	0.013	0.999						
Cu	—0.079	0.019	0.112	—0.018	0.019	1.000					
Ni	—0.077	0.053	0.033	—0.088	0.016	0.837	0.999				
Co	—0.108	—0.058	0.082	—0.062	—0.065	0.720	0.703	1.000			
Sr	—0.203	—0.236	—0.144	—0.244	—0.099	—0.123	—0.176	—0.057	1.000		
Ti	—0.024	—0.129	0.165	0.041	—0.140	—0.148	—0.364	0.054	0.113	0.999	
Zr	—0.014	0.175	0.086	0.233	0.049	0.087	0.077	0.117	0.153	0.318	1.000

3. elements, whose contents are most frequently 10 to 100 g . t^{-1}: Cr, Cu, Ni, Sr, B (B was not identified in 9 samples);

4. elements present in amounts < 10 g . t^{-1} and in trace amounts: Co, Pb, Sn, Ga (Sn and Ga occur in trace amounts in most samples or were absent altogether).

The survey and division of the elements into the groups show the high variability of their contents, especially of the elements in parentheses, which display differences of up to 1—2 orders of magnitude. Generally, it can be stated that except for Zr none of the elements studied has a uniform content in the black slates of the Malé Karpaty crystalline complex. The average values more or less approximate the average values given by different authors for similar rocks.

In Table 9 there are average values of the elements studied (in g . t^{-1}) from 76 spectral analyses and their statistical parameters.

In graph 4 two fields of correlation projections are distinguishable. One shows the positive relationships between the element contents and the other indicates area of Cu decrease in rocks. The graph reveals that some rock groups with a higher contents of sulphides occurring outside the productive zones of the Pezinok—Pernek crystalline complex also belong in this field (see the beginning of Chapter II).

The study of the relationships between the elements studied issued from the correlation coefficients, computed from the results of the quantitative SPA method on a computer WANG 2200 B. The correlation matrix is given in Table 10. The highest correlation coefficient $r = 0.837$ was obtained for the Cu — Ni pair, and a fairly high cor. coefficient for the Cr — V pair. A good correlation between these elements is obviously due to their similar geochemical properties. Correlation graphs of Cu/Ni and Cr/V are shown in Figs. 4, 5.

In order to illustrate the interrelationships between the elements studied, we have constructed a dendrogram which expresses the hierarchy of the groups computed. Figure 6 presents the connections of element groups at a certain correlation level. The closest connection exists between V and Cr and in the group of Cu, Ni and Co. Boron and strontium are located in the scheme separately and do not correlate with any other element.

As we thought it advisable to take into consideration also negative correlations, we have compiled a Table 11 of geochemical affinity of the elements in the Malé Karpaty black slates.

To every element in the Table, related elements are ranged according to the decreasing value of the correlation coefficient. The elements under the line are negatively correlated with the element in the heading. For example, in the case of Cu the geochemical affinity decreases from Ni to Pb (positive correlation coefficients) and from Ti to Ba (negative correlation coefficients).

The correlation of the elements studied to organic carbon has been determined by arranging the samples according to the decreasing content of C_{org} content, and the contents of microelements have been added to the corresponding values. As already stated by many authors, V shows a definite positive correlation with organic carbon. The B and Cu contents have not shown a demonstrable relationship; they vary greatly with respect to the content of organic carbon. From the computed correlation coefficients of C_{org} and the

Table 11

Geochemical affinity of the elements studied in the black slates of the Malé Karpaty crystalline complex

V	Cr	Cu	Ni	Co	Ti	Zr	Pb	Ba	Sr	B
Cr	V	Ni	Cu	Cu	Zr	Ti	V	V	**Ti**	Ba
Ba	Ba	Co	Co	Ni	Cr	Ba	Cu	Zr	Ba	**V**
Zr	Ti	Cr	Zr	Cr	Sr	V	Ni	Cr	V	Sr
Pb	Cu	Zr	V	Zr	Co	Ni	**Ba**	B	B	Co
Ni	Zr	V	Cr	**Ti**	**Ba**	Cu	Ti	Ti	Ni	Cu
Cu	Co	**Pb**	**Pb**	B	Ni	Cr	Sr	**Pb**	Zr	Ni
B	**Ni**	Ti	Ti	Pb	Cu	**Co**	Co	Sr	Cr	Cr
Sr	Sr	Sr	Sr	Ba	Pb	Sr	Zr	Ni	Cu	Ti
Ti	B	B	Ba	Sr	V	Pb	B	Co	Pb	Pb
Co	Pb	Ba	B	V	B	B	Cr	Cu	Co	Zr

elements examined, the approximate scheme of geochemical affinity of C_{org} to individual elements in the dark slates can be compiled:

$$V > Ni > Cr > Ba > Pb > B > Ti > Sr > Co > Zr > Cu$$

The analysed samples of the Malé Karpaty black slates have been grouped, from the regional point of view, with three areas: the Modra—Orešany area comprising the rock samples from the northern vicinity of the Pezinok—Pernek crystalline complex, the Bratislava area to the south of the central Pezinok—Pernek area. For every sample examined the arithmetic mean, standard deviation and, for the purpose of comparing the variability in individual areas, also the variation coefficient (Table 12) were computed. It is apparent at the first sight that Ti and Zr show the minimum variability of contents (minimum variation coefficients) in the individual areas. Ni in samples from the Pezinok—Pernek area has four times greater concentration than Ni from the other two areas, and Cu twice as great. This is due to that the samples from the Pezinok—Pernek area were richer in sulphides (pyrite, pyrrhotite). The V contents in samples from this area are also several times higher.

In the second stage of investigation also the geochemistry of the analysed elements has been studied, both in samples from the productive pyrite-bearing zones and from the localities outside these zones. Additionally, ten samples divided into a heavy and a light fraction on a separation table permited to determine accurately the mode of bond of the element in rocks. The two sets of samples have been evaluated statistically and graphically as well. The comparison of Tables 13 and 14 shows a surprisingly high increase in the average contents of some elements in samples from the productive zones relative to their contents in samples from the localities outside these zones. The increase

Table 12

Basic statistical characteristics of the elements studied from the areas of sampling localities (Pezinok — Pernek 40 samples, Modra — Orešany 23 samples, Bratislava 13 samples, content in g . t^{-1})

Element	Pezinok—Pernek			Modra—Orešany			Bratislava		
	$\bar{x}$	S	V %	$\bar{x}$	S	V %	$\bar{x}$	S	V %
B	40	33	82	58	78	134	35	32	91
V	545	698	128	232	230	99	171	155	90
Cu	102	84	82	54	71	131	50	40	80
Ni	142	142	100	34	70	70	35	13	37
Co	9	6	66	6	4	66	7	3	43
Cr	143	137	96	83	55	66	77	31	40
Ba	5238	3784	72	5519	1660	30	3097	3970	128
Sr	185	132	71	117	73	62	318	484	152
Ti	4321	1648	38	5094	1525	30	4623	1507	32
Pb	7	5	71	6	7	116	18	40	222
Zr	108	41	38	133	53	40	132	43	32

in V and Cu is 2.5 fold and in Ni almost 7 fold. The factors of enrichment (in relation to Taylor's values of clarkes of the earth's crust) of these three elements in the productive zones are: V — 3.7, Cu — 2.1 and Ni — 2.8.

From this finding it was inferred that V, Cu and Ni are most appropriate for the discrimination of dark slates of the productive zones from other dark slates of the Malé Karpaty crystalline complex. In order to verify this assumption, discriminant analysis was made.

The discriminant analysis of the samples of Malé Karpaty dark slates was computed after a programme devised by I. Jedlička on a WANG 2200 B computer. The problem to be solved related to the separation of groups of individuals divided according to a certain set of features, i.e. to classify samples in categories previously defined and differentiated. At first, two defined groups were established, a group of 58 samples from the productive zones and a group of 44 samples from the localities outside these zones. After several trials, a 78 % accuracy has been achieved, i.e. 80 samples out of 102 samples were ranged correctly, which practically agrees with the correctness given in the literature (e.g. Miller — Kahn, 1962). The discriminant analysis substantiated the assumption that the contents of V, Cu and Ni are most helpful in distinguishing between the dark slates of the productive zones and the other Malé Karpaty slates (Khun, 1980).

In the second investigation stage the geochemistry of the analysed samples was studied with the objective to recognize the bond of individual elements in black slates.

Table 13

Basic statistical characteristic of the elements studied from the productive zones (58 samples, content in g . t^{-1})

Element	$\bar{x}$	Median	S	V (%)	Variation span	Most common content
B	47	35	59	127	0—330	0—30
V	507	380	792	156	79—6000	100—200
Cu	118	92	107	91	7.9—525	0—50
Ni	211	106	224	106	10—850	0—50
Cr	127	50	155	123	35—1000	50—100
Ba	3562	805	4076	114	80—10 000	10 000
Sr	122	105	93	76	5—590	0—50
Ti	3673	3625	1638	44	288—10 000	3000—4000
Pb	10	4	9	96	0—45	0—10
Zr	112	112	54	46	30—282	75—100

Table 14

Basic statistical characteristics of the elements studied from the rocks outside the zones (44 samples, content in g . t^{-1})

Element	$\bar{x}$	Median	S	V (%)	Variation span	Most common content
B	43	36	63	147	0—410	20—60
V	198	115	206	104	30—760	60—120
Cu	48	30.5	58	122	3.6—166	0—15
Ni	31	29.5	20	66	10—135	20—40
Cr	76	74	47	62	st.—295	75—100
Ba	4614	955	5132	111	83—10 000	10 000
Sr	214	130	318	148	st.—1950	50—100
Ti	4764	5050	1520	32	890—7900	5000—6000
Pb	10	4	24	237	0—155	0—10
Zr	117	121	53	45	30—282	100—150

Boron

In the rocks studied boron is associated only with the mineral substance, obviously in the sericitized feldspars and in muscovite. It has not displayed any relation to the organic matter. The principal concentrator of boron in the

rocks, viz. tourmaline, has not been identified microscopically. In samples divided into light and heavy fractions boron showed the tendency to concentrate in the light fraction, which would confirm the absence of tourmaline. The calculated average boron contents in the Malé Karpaty black slates are low compared with the values given in the literature, approximately attaining half these values. According to H a r d e r the reduction of boron contents is associated with diagenetic and chiefly with metamorphic processes, which interpretation can also be applied to the black slates of the Malé Karpaty region. By the effect of contact metamorphism, for example, the lattice of clay and micaceous minerals is disturbed and the released boron is partly removed by water vapour. H a r d e r (1961) reports a decrease in boron content from 165 g . t^{-1} in unmetamorphosed red clay to 32 g . t^{-1} in metamorphosed bleached clay. The decrease in boron may alternatively be interpreted in terms of the sericitization of plagioclases. B a r s u k o v (1961) analysed plagioclases taken from one rock with different degrees of sericitization and found that boron contents decreased with the increase in the intensity of sericitization. The low boron contents (36 g . t^{-1}) in the black slates of the Malé Karpaty crystalline complex are obviously due predominantly to metamorphic processes.

Vanadium

Vanadium plays an important role in the processes of surficial alteration on account of its biophile character. In the reducing sedimentary environments where bituminous shales originate, vanadium accumulation often develop. This finding can also be applied to black slates of the Malé Karpaty crystalline complex, in which a marked relationship between vanadium and organic matter has been established. The association of vanadium with organic matter has been supported by its concentration predominantly in the light fraction of samples. The contents of vanadium in the Malé Karpaty black slates varies between 30 and 6000 g . t^{-1}. The average content in samples from the productive zones was substantially higher (452 g . t^{-1}) than in other areas. The increase is due to higher C_{org} in these zones and lends additional support to the assumption that vanadium is preferentially bond to organic matter and, obviously, in its reduced form V^{3+}, because in the environment enriched in C_{org} V^{5+} becomes reduced to V^{3+}. The high contents of vanadium in samples from the productive zones make it a characteristic trace element, markedly facilitating the discrimination between the samples from the localities in productive zones and those located outside them.

Copper

Owing to its high affinity to sulphur, copper in rocks generally occurs as sulphate or sulphide compounds. It is universally present in sediments. The increased Cu contents in samples from the productive zones (142 g . t^{-1}, compared with 91 g . t^{-1} in the whole set) are produced by increased amounts of sulphidic minerals, which is also indicated by the concentration of copper in the heavy fraction.

From their chalcographic studies C a m b e l — J a r k o v s k ý (1967) infer that the predominant part of copper in the Malé Karpaty pyrites occurs in the

form of chalcopyrite or other Cu minerals forming microscopic and submicroscopic inclusions. Under changed physico-chemical conditions these minerals may form mixed crystals with the pyrite. In this way copper together with V and Ni greatly assists in discriminating between the samples from the productive zones and those from other areas.

Nickel

Nickel is an important siderophile element. Krauskopf (1955) gives a value range from 20 to 300 $g.t^{-1}$ for the black shales. For the Malé Karpaty black slates a value of 114 $g.t^{-1}$ was computed for the whole population of samples. The increased values of Ni in the productive zones are obviously produced by the presence of sulphidic minerals — pyrite and pyrrhotite. According to Cambel and Jarkovský (1967) nickel is bound in pyrite and pyrrhotite isomorphically. The bond of Ni in these sulphidic minerals is also confirmed by the concentration of it in the heavy fraction of samples divided on a separation table. As concerns the mineralization, an interesting feature is the concentration of Ni in amphibolic rocks of the Malé Karpaty Mts. (Cambel — Kupčo, 1965). Recent studies have revealed that the Malé Karpaty pyrites have higher Ni and Cu than pyrites of other Západné Karpaty deposits or of sedimentogenic sulphide deposits in other world countries. This fact might be accounted for by a relatively high content of nickel in the amphibolic rocks of the Malé Karpaty region. The above-cited authors have determined a Ni content of 199 $g.t^{-1}$ in the basic amphibolites, which are most widespread amphibolic rocks in the Malé Karpaty. From this they inferred that the amphibolic rocks of the Malé Karpaty and geosynclinal submarine basic volcanism associated with them might be a source of a relatively high Ni content in the pyrites.

Chromium

The geochemistry of chromium in the Malé Karpaty black slates is complicated. According to the literature, the most probable interpretation would be the presence of amphibolite pyroclasts in the black slates studied. However, Cambel and Kupčo (1965) determined and average content of 282 $g.t^{-1}$ for the Malé Karpaty amphibolites and 435 $g.t^{-1}$ for those of the Harmónia Group. These values are substantially higher than the value of 92 $g.t^{-1}$ established for the black shales. To explain the possibility of chromium concentration in the light fraction we may point out its good correlation with vanadium, which is markedly concentrated in the light fraction in organic matter, and its tendency to correlate with organic matter. Polanski and Smulikowski (1971) reported that in rock-forming silicates chromium occurs as Cr^{3+} replacing Fe^{3+} and occasionally also Al^{3+} (e.g. in muscovite).

Barium

In the Malé Karpaty black slates the Ba contents are extraordinarily increased, attaining 2667 $g.t^{-1}$, which even exceeds the maximum value for black shales given as 2500 $g.t^{-1}$ by Krauskopf (1955). The distribution of barium

is highly irregular in all areas studied. The high contents of barium are difficult to explain satisfactorily. The potassium feldspars, which might be regarded as plausible sources, have so low K contents that such high concentrations of barium (above 10 000 g . t^{-1}) in them can hardly be presumed. Barium is known to be associated with carbonates, and its occurrence in hydrothermal veins in the crystalline rocks and increased Ba in metamorphic schists also should be taken into consideration. Therefore, barium must be regarded as a primary component originating in a higher degree already during sedimentation.

Strontium

In the rocks studied strontium is probably contained in feldspars; its marked correlation with carbonates, described in the literature, may be applied to the Malé Karpaty crystalline rocks. The average content is 168 g . t^{-1}. The sample K-3 with a Sr content of 1950 g . t^{-1} is rich in calcite. Strontium may also accompany barium.

Titanium

The titanium contents in samples from the different areas vary little, as is demonstrated by low coefficients of variation. It is obviously present in accessory rutile, which was determined microscopically. The predominant part of titanium appears to be associated with iron in various minerals. The average content of titanium in the rocks studied was 3851 g . t^{-1}.

Lead

Lead was found in most of the samples in trace amounts only and therefore it is not applicable in discriminating between samples from the productive zones and samples from other areas. Cambel and Jarkovský (1967) describe the occurrence of lead in the Malé Karpaty pyrites in the form of a heterogeneous mineral. The frequent presence of trace Pb can be explained, at least partly, in terms of its easy migration under the metamorphic effects of granite magma.

Zirconium

Turekian — Wedepohl (1961) give the average content of zirconium in shales as 160 g . t^{-1}. The Zr contents in black slates of the Malé Karpaty crystalline complex are uniform, ranging about 100 g . t^{-1}. Zirconium is concentrated chiefly in accessory zircon (it concentrated in the heavy fraction) but it is also found disseminated, replacing other elements in the minerals.

II.9. Trace elements in slates classified according to established criteria

In this section, the evaluation is based on the assessment of average contents of the elements in individual sets and their correlation. The results of analyses are represented in histograms. Arithmetic means are compared graphically.

Table 15

Basic statistical parameters of trace elements of the whole set of black slate samples from the Malé Karpaty crystalline complex

Set of all samples				
Element	AM	AD	CV	GM
B	36	49	138	25
V	358	527	147	210
Cu	91	146	161	42
Ni	114	205	179	49
Co	13	14	114	7
Cr	92	107	116	69
Ba	2667	4200	157	963
Sr	168	215	128	102
Ti	3851	1846	48	3233
Zr	125	58	46	108
C_{org}	1.5	2.5	160	1.1
n = 190				

Explanations: AM — arithmetic mean; AD — arithmetic standard deviation; CV — coefficient of variation in per cent; GM — geometric mean; n — number of analyses. Contents of trace elements in $g.^{-1}$, C_{org} in %.

Table 15 presents the whole population of 190 samples. The set comprises all samples that were chosen for the geochemical study of slates of the productive zones and slates with a perceptible content of organic component, which occur outside these zones. The Table contains the values of arithmetic mean (AM), standard deviation (AD), coefficient of variation (CV) and geometric mean (GM).

Table 16 lists the statistical values of microelement contents in sets arranged according to the content of C_{org}, and in Table 17 the sets are grouped according to grain-size and grade of metamorphic crystallization of the rocks analysed. The contrasting sets of rocks included in Tables 15 and 16 have different geochemical and petrological picture. For example, the increase of C_{org} in slates results in the increasing amount for those elements which decrease with the increasing grade of metamorphism (Table 17), i. e. of recrystallization of the rocks. The metamorphosed rocks are divided into two groups: one comprises rocks affected by low-grade metamorphism, and the other rocks of medium- and high-grade metamorphism. Graph 7 representing the relationship between metamorphism and element content, includes values computed for all 190 dark slates studied (column B), generally little recrystallized. The graph shows that with the increase in metamorphic grade the content of the following elements rises: B, Cr,

Table 16

Basic statistical parameters of trace elements in the analysed samples of black slates, arranged according to the C_{org} content.

	Content of organic carbon											
	C_{org} < 0.5 %				C_{org} 0.5 — 3 %				C_{org} > 3 %			
	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM
B	28	28	100	19	37	52	143	24	51	73	143	32
V	203	257	127	133	257	235	91	189	824	1024	124	540
Cu	63	94	149	34	124	230	185	50	90	83	92	50
Ni	57	68	119	38	140	319	228	48	180	235	130	69
Co	13	13	100	8	13	14	108	7	9	10	108	4
Cr	75	43	58	63	108	106	99	78	142	209	147	96
Ba	1870	3446	184	785	3787	5089	134	1260	4496	5206	116	1668
Sr	224	291	130	148	168	147	87	121	77	71	90	49
Ti	4330	1550	36	4078	4276	1724	40	3802	3038	2004	66	2252
Zr	150	48	32	141	126	57	45	114	120	46	38	107
C_{org}	0.2	0.1	51.5	0.1	1.2	0.7	64	0.7	5.7	2.7	48	5.1
	n = 71				n = 41				n = 32			

For explanations see Table 15.

Sr, Zr, Co and the contents of other elements decrease or do not change appreciably (Ba, Ni, Cu). In samples arranged according to the increasing C_{org} content (Fig. 7) the elements B, V, Cu, Ni, Cr and Ba increase in amount with the increase in carbonaceous matter. The contents of Co, Sr, Ti, Zr and others decrease. It is thus apparent that the organic matter intensively captures especially V, Ba, Ni, Cr, Ti and partly also Cu. The concentration of Cr, Zr, Co and Fe declines with the increase in organic matter.

With the increase in grain-size (Table 17) rises the amount of most of the elements that displayed an increase with the rising grade of metamorphism or other alterations, because in a substantial part of samples the crystallinity increases particularly in results of higher metamorphism grade. This is indicated by the rise of Ti, Cu, Sr, Co, Zr in coarse-grained rocks and a decrease of B, V, Ni, Ba, Cr and C_{org} in finer-grained rocks. Table 18 and Fig. 8 present the geochemical characterization of samples arranged according to the content of sulphides. It is apparent that with the increasing content of pyrite (sulphides) in the individual sets, the amount of organic matter (C_{org}), B and V increases, but in the group of ores V, Cu, Ni, Cr and Ba decrease. But in slates of "B" type Ba increases. The contents of Sr, Ti and Zr decrease. This suggests a certain geochemical specificity of ore samples (type C) when compared with

Table 17

Basic statistical parameters of trace elements in the analysed samples of black slates arranged acording to the grain-size distribution and grade of metamorphism

	Granularity								Metamorphism rank							
	Fine-grained				Medium-grained				Epi-				Mezo- Kata-			
	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM
B	46	66	143	28	35	45	130	21	42	58	138	25	39	37	122	19
V	611	973	159	325	288	291	101	186	376	644	171	212	341	341	100	210
Cu	83	85	102	45	95	162	171	41	81	119	147	39	92	112	122	46
Ni	119	183	154	46	115	215	187	51	117	174	149	51	96	150	156	47
Co	12	12	100	5	13	15	118	6	13	16	126	7	12	11	90	7
Cr	119	184	154	84	83	73	88	64	91	122	134	67	93	85	91	72
Ba	4107	5080	124	1371	2301	3868	168	889	2842	4413	155	947	2623	4070	155	1085
Sr	145	171	118	83	167	221	132	105	173	264	152	95	150	108	72	103
Ti	3472	1932	56	2777	3980	1840	46	3376	3794	2018	53	3064	4005	1609	40	3563
Zr	115	51	45	101	123	59	46	110	125	63	50	105	124	50	40	112
C_{org}	2.8	3.6	128	1.6	1.1	1.9	163	0.6	1.1	2.0	175	0.9	2.0	2.8	142	1.1
	n = 39				n = 144				n = 104				n = 79			

For explanations see Table 15.

Table 18a

Basic statistical parameters of trace elements in the analysed samples of black slates arranged according to the content of sulphides (samples from the Pezinok—Pernek crystalline complex)

	Sulphide content											
	Type A				Type B				Type C			
	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM
B	37	56	150	17	40	48	120	19	41	48	118	20
V	262	277	106	170	584	959	164	307	473	298	63	398
Cu	67	98	147	34	119	128	108	61	372	416	112	221
Ni	66	89	135	39	120	122	101	56	752	489	65	544
Co	11	11	100	5	14	15	112	6	31	31	100	18
Cr	84	71	84	67	125	188	150	81	75	34	45	67
Ba	2216	3820	172	860	4165	5155	124	1623	1704	3881	228	410
Sr	187	250	133	119	136	117	86	89	33	29	87	26
Ti	4087	1551	38	3646	3957	2076	52	3424	919	1180	128	615
Zr	132	60	45	114	128	50	39	117	128	50	39	117
C_{org}	1.4	2.5	181	0.7	1.7	2.0	118	1.1	2.2	2.3	105	
	n = 110				n = 41				n = 9			

Explanations: type A — slates without visible content of sulphides; type B — slates with macroscopically visible sulphide content; type C — sulphide (pyrite) ore. For other explanations see Table 15.

mineralized slates (type B) and pyrite-less slates (type A). The ores display mixed geochemical characteristics, caused by a gradual increase in organic matter from type A through B to type C. This trend is moreover combined with metamorphic activity of various grades. The amount of sulphides produces a different geochemical pattern. The group of ores analysed by the authors show different stages of metamorphic alteration.

The last three columns of Table 18 comprise the sets of rock samples taken only from the productive zones of the Pezinok—Pernek crystalline area. The complete set of 190 samples divided into three groups is represented in the first three columns: the rocks depleted in sulphides form group A, sulphides-bearing rocks from group B and pyrite ores group C.

The slates of the productive zones, in relation to the rocks arranged in the first three columns (Table 18) show an increased concentration of some elements, e.g. B, V, Cu, Ni and Ba, a lower content of Ti, and unchanged amounts of Co, Cr, Zr and C_{org}. As the average contents of C_{org} are approximately identical in the sets from the productive zones, the effect of C_{org} on the contents of elements has been excluded by this re-distribution of analyses. It has also revealed that the rocks of productive zones, compared with the complete set arran-

Table 18b

	Pezinok — Pernek crystalline area											
	Productive zones as a whole				Productive zones-type A				Productive zones-type B+C			
	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM
B	48	58	120	26	46	62	135	22	48	53	110	25
V	452	370	82	311	405	348	86	275	514	392	76	363
Cu	142	147	104	80	115	138	120	59	172	156	91	109
Ni	179	212	118	91	115	127	110	69	258	271	105	123
Co	17	17	100	10	16	13	78	11	18	21	115	10
Cr	104	89	85	82	104	97	94	79	101	77	76	82
Ba	2521	4069	161	914	1231	2026	164	664	3828	5060	132	1319
Sr	148	205	138	84	190.	262	138	111	98	83	85	61
Ti	3481	1855	53	2778	3672	1733	47	3157	3166	2008	63	2282
Zr	107	50	47	94	103	54	90	26	110	45	41	100
C_{org}	2.0	2.4	118.4	1.2	1.9	2.4	124	0.7	2.1	2.5	115	1.5
	n = 74				n = 40				n = 34			

For explanations see Tab. 18 a.

ged according to sulphide contents, have higher contents of the elements examined, particularly those from the Fe group and U, Sb, As, Hg, Zn and others (see Chapter III).

The sets of samples in Table 19 are grouped on the basis of regional and stratigraphic criteria.

This Table and Fig. 9 show that the element contents in the individual sets are controlled by the grade of metamorphism: the oldest and most intensely metamorphosed rocks have the lowest contents of microelements as compared with the lower-metamorphosed rocks, specially if these contain increased amounts of carbon and sulphides.

The Harmónia Group has lower or equal contents of microelements as the crystalline schists in its basement, except for the schists of the Bratislava massif. The contents of V, Cu, Ni, Co, Cr and Sr are decreased and those of Ti and Ba are increased. As in contrast to other schist types, the slates of the Harmónia Group contain, on the average, 4.30 ppm U and 9.20 ppm Th, it may be stated that the dark rocks of the Harmónia Group are geochemically identifiable. The younger, Mesozoic dark marly rocks, Jurassic Mariatal Shales and Lower Triassic (Lias?) shaly limestones contain still lower amounts of elements of the Fe group (V, Cu, Ni, Cr, Co and C_{org}) and show a high increase in Ba, Sr, and Ti contents.

Table 19

Basic statistical parameters of trace elements in the black slate samples from the crystalline basement and in samples arranged on stratigraphic basis

	Subjacent crystalline area											
	Pezinok—Pernek crystalline area outside productive zones				Bratislava area				Modra—Orešany area			
	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM
B	19	17	89	10	27	27	100	15	73	165	224	54
V	476	1156	242	183	187	254	136	129	113	28	25	110
Cu	54	24	138	29	95	271	284	29	27	21	76	21
Ni	73	101	138	34	112	372	331	34	29	10	34	27
Co	13	16	125	6	11	14	122	5	8	7	90	6
Cr	123	227	184	70	69	33	46	58	58	21	36	55
Ba	3490	4796	137	1360	2258	3850	170	907	2415	4697	194	830
Sr	217	186	85	152	256	383	150	140	156	105	67	125
Ti	4618	2077	45	4264	3893	1463	37	3503	4410	1320	30	4254
Zr	151	53	36	139	148	42	28	143	187	53	28	182
C_{org}	1.3	3.0	224	0.8	1.0	1.8	180	0.3	1.2	2.1	170	0.4
	n = 26				n = 24				n = 6			

	Stratigraphy											
	Subjacent crystalline area as a whole				Harmónia Group				Younger formations (Triassic)			
	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM
B	39	58	151	22	30	19	62	21	38	47	122	24
V	419	612	146	245	260	260	100	170	123	35	28	119
Cu	115	171	148	54	42	56	132	26	59	54	91	37
Ni	151	242	160	67	45	45	100	30	35	9	26	34
Co	15	16	106	7	7	8	111	3	10	7	64	8
Cr	102	123	121	77	73	51	70	57	77	31	40	72
Ba	2456	3977	162	926	2977	4497	151	1032	4791	5971	125	1518
Sr	178	245	137	102	121	83	68	92	234	153	65	190
Ti	3757	1914	51	3089	4165	1826	44	3575	4460	1222	27	4309
Zr	121	53	44	108	125	66	53	98	163	61	37	154
C_{org}	1.8	2.5	140	1.1	0.9	2.2	248	0.4	0.4	0.4	100	0.3
	n = 130				n = 47				n = 8			

For explanations see Table 15.

In Table 20 the sets of samples are arranged according to the contents of some key minerals, or according to the manifestations of hydrothermal and superimposed tectonic processes; the values are represented in Fig. 9.

The average contents of microelements compiled in Table 20 allow to draw the following conclusions: The classification of rocks based on the greater or lesser representation of quartz does not provide marked differences in the average contents of elements. Only V and C_{org} contents are lower in the rocks having less quartz and, conversely, Ni, Sr and Ti show a higher concentration in these rocks. The values of the remaining elements remain essentially constant.

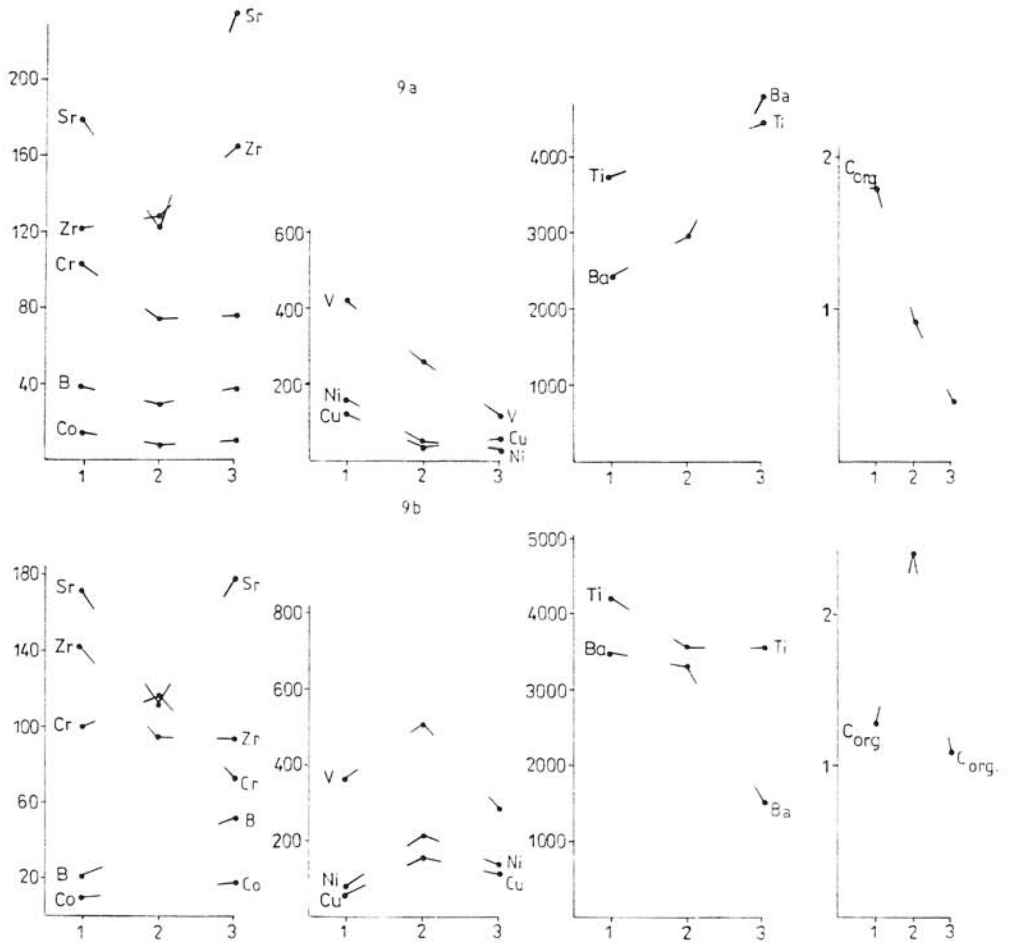


Fig. 9. Average contents of trace elements in the samples of black slates arranged according to stratigraphy (9 a) and mineralogy (9 b).

Explanations: Contents in g . t^{-1}. 9 a: 1 — crystalline basement, undivided; 2 — Harmónia Group; 3 — younger formations, Mesozoic. 9 b: 1 — increased content of biotite, garnets and feldspars; 2 — increased amphibole content; 3 — increased content of carbonates.

Table 20

Basic statistical parameters of trace elements in the black slate samples arranged according to mineralogy

	Silica visually								Biotite, garnet				Amphibole			
	more				less				feldspar							
	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM
B	38	49	129	25	36	55	151	22	21	23	113	16	39	43	124	24
V	429	655	153	234	263	251	96	185	371	790	213	172	506	365	72	366
Cu	90	130	145	40	100	181	180	48	67	94	141	36	164	241	147	75
Ni	103	158	153	44	144	277	193	62	75	121	160	40	217	340	157	93
Co	11	15	131	7	14	14	99	8	10	10	100	8	14	14	104	8
Cr	89	124	138	66	98	83	85	75	100	153	153	71	116	104	89	90
Ba	2735	4144	151	1070	2858	4507	158	919	3508	4797	137	1333	3352	4498	134	1257
Sr	133	167	125	82	210	266	127	138	170	136	80	121	115	111	97	75
Ti	3481	1680	48	2900	4444	2045	46	3774	4238	1801	42	3820	3530	2083	59	2689
Zr	132	55	45	107	123	60	49	105	140	53	38	129	95	52	54	82
C_{org}	1.9	2.7	143	0.9	0.9	1.8	189	0.5	1.3	2.0	150	0.8	2.4	2.9	120	1.5
	n = 107				n = 68				n = 64				n = 40			

For explanations see Table 15.

Table 21

Basic statistical parameters of trace elements in samples of black slates affected by hydrothermal alteration, mylonitization and weathering, and in samples with a higher content of carbonates

	Hydrotermal alterations				Mylonitization, weathering				Higher portion of carbonates			
	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM
B	52	69	134	30	57	87	153	33	51	65	128	28
V	293	315	107	200	291	296	101	194	297	302	102	193
Cu	113	138	122	57	103	127	123	54	107	150	140	47
Ni	81	94	117	48	76	104	137	41	126	180	142	63
Co	16	18	109	10	12	18	157	6	18	22	120	11
Cr	93	73	78	71	70	58	82	52	74	55	74	58
Ba	3738	4979	133	1358	2306	4092	177	874	1554	2891	186	625
Sr	154	79	51	124	145	101	69	94	178	326	184	105
Ti	4259	1869	34	3832	3890	1556	40	3329	3522	1853	53	2838
Zr	131	59	45	118	139	62	45	112	93	59	63	73
C_{org}	1.6	2.8	171	0.9	1.3	2.3	132	0.8	1.1	2.6.	221	0.6
	n = 24				n = 21				n = 33			

For explanations see table 15.

The comparison of the sets of samples bearing biotite, garnet and feldspar with amphibole-bearing rocks (metatuffs and metatuffites) shows great differences in the contents of trace elements. The amphibole-bearing rocks exhibit increased contents of B, V, Cu, Ni and C_{org} (obviously some pyrite ores are included), and smaller amounts of Sr, Ti and Zr. The contents of other elements are unchanged.

The set of samples with increased carbonate contents (Table 21) is obviously chemically influenced by hydrothermal activity; in relation to the biotite- and feldspars-bearing rocks it contains higher B, Cu, Ni and Co amounts and lower Cr, Ba, Ti and C_{org}. The Sr contents remain unchanged. These data point to a striking peculiarity of the set of samples with an increased content of carbonates.

Between the sets of hydrothermally and tectono-metamorphically altered rocks there are no differences in the content of microelements except for chromium and barium, which occur in mylonitized rocks in minor amounts. It should be remarked that the hydrothermally altered rocks and rocks with increased contents of carbonates display increased values of other elements from the group of polymetals, which are not discussed here.

The histograms presented at the end of Section II. 9 are constructed so as to show the frequency of content values of the elements grouped with the individual rock populations, especially those which are compared in graphs and tab-

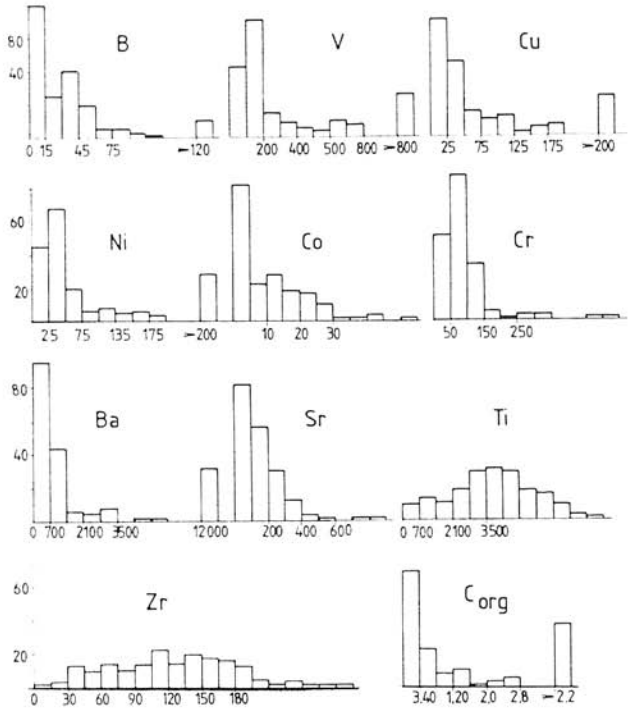


Fig. 10. Histogram showing the distribution of trace elements frequency in the examined samples of the whole set (190 samples). Contents in g . t^{-1}.

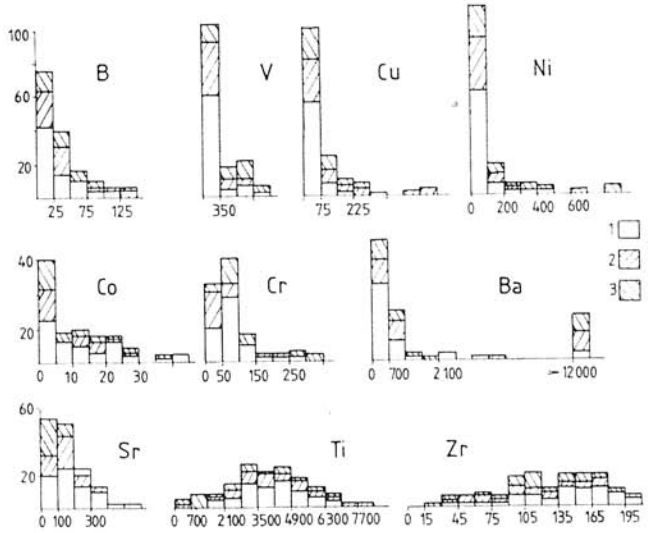


Fig. 11. Histogram of distribution of trace elements frequency in the rocks studied, divided according to the content of C_{org}.

Explanations: Contents in g . t^{-1}. 1 — C_{org} content below 0.5 %; 2 — C_{org} content between 0.5 and 3 %; 3 — C_{org} content above 3 %.

les. In Fig. 10 the entire set undivided into subpopulations is included. The frequency values in the sets arranged according to the contents of organic matter are given in Fig. 11, according to sulphide contents (Fig. 12), and according to the representation of the studied minerals of discriminations significance (Fig. 13).

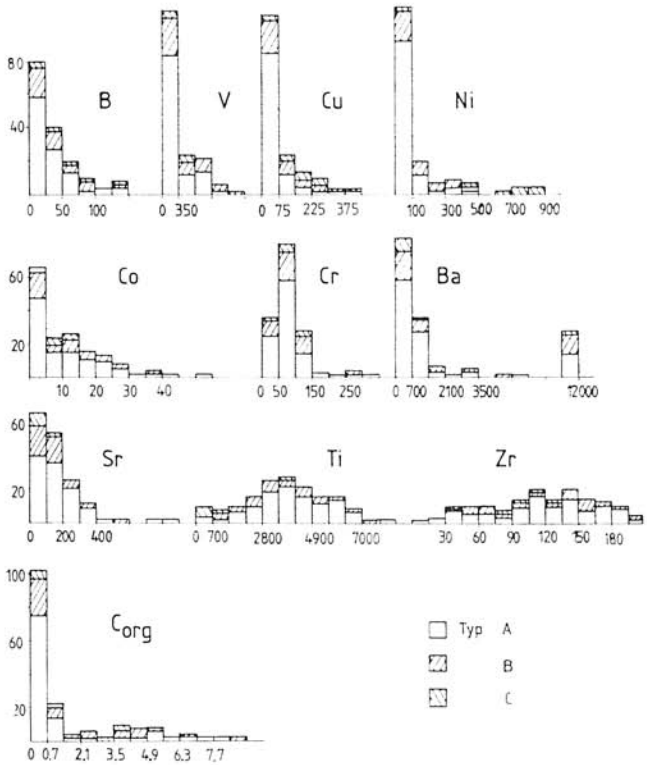


Fig. 12. Histogram of distribution of trace elements frequency in the rocks studied, arranged according to the content of sulphides.
Explanations: Contents in $g \cdot t^{-1}$. For types A, B, C see Fig. 8.

II.10. Macroelements in black slates of the Malé Karpaty Mts.

We had at our disposal 84 incomplete silicate analyses for the determination of seven elements (O, Si, Na, Al, Fe, Mg), which were made in the Geofyzika, nat. corp., Brno, using the INAA method by means of neutron activation in laboratory generator analyst Ing. J. Bartošek, CSc.). The results in cation form are presented in the catalogue, and for tabular presentation they were recalculated into oxides. Potassium was determined by γ — spectrometry in the Geological Inst. of the Slovak Acad. Sci., Bratislava (analyst RNDr. V. Kát-

lovský, CSc.). The data have been published in the paper of Cambel — Kátlovský — Khun (1981). The results of statistical treatment (arithmetic means, standard deviations, coefficients of variation and geometric means) are in Tables 22 to 28 for individual groups.

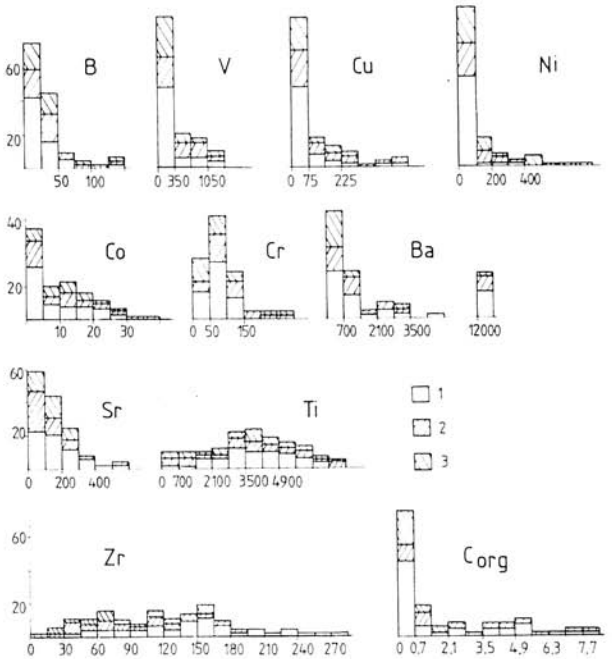


Fig. 13. Histogram of distribution of trace elements frequency in the rock studied, arranged according to mineralogical composition.
Explanations: Contents in $g.t^{-1}$. 1 — increased content of biotite, garnet and feldspars; 2 — increased amount of amphibole; 3 — increased amount of carbonates.

Table 22 lists average values from 84 samples of the black slates of the Malé Karpaty crystalline complex. The contents of macroelements compare well, for example, with black slates from Outokumpu Finland (Peltola, 1960) or black slates from the Lower Silurian of the Barrandian (Kukal, 1961). The distribution of macroelements in the black slates studied is mainly controlled by the detrital fraction and less by diagenetic minerals such as pyrite and carbonates. No significant correlations between the macroelements have been established, and correlations with trace elements have not been carried out.*

Table 23 shows a parallel increase of SiO_2 with the increase in the C_{org} content. This relationship has already been reported in several papers. The Al_2O_3/C_{org} ratio is inversely correlated. In some cases this may be due to the lyditic

* For the lack of space the correlation matrices are not included in the paper.

Table 22

Basic parameters of the major elements in black slate samples

	Set of all samples			
	AM	AD	CV	GM
K_2O	1.32	1.32	100	1.13
SiO_2	55.85	15.62	28.1	51.15
Na_2O	2.55	4.29	170.2	2.12
Al_2O_3	11.84	5.45	45.8	9.96
Fe_2O_3	7.58	7.29	95.9	5.57
MgO	2.82	3.32	117.5	2.54
	n = 84			

Explanations: AM — arithmetic mean; AD — arithmetic standard deviation; CV — coefficient of variation in per cent; GM — geometric mean; n — number of samples. Contents in per cent. F_2O_3 represents the Fe_{total} value.

Table 23

Basic statistical parameters of major elements in the examined samples of black slates, arranged according to C_{org} content

	Content of organic carbon											
	C_{org} < 0.5 %				C_{org} 0.5—3 %				C_{org} > 3 %			
	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM
K_2O	1.32	1.44	109.3	1.10	1.32	1.44	109.3	1.09	1.20	1.44	118.5	1.08
SiO_2	55.21	10.27	18.6	54.14	53.71	17.12	32.1	50.07	60.13	16.91	28.1	50.07
Na_2O	2.81	1.21	46.4	2.41	2.14	1.47	66.4	2.12	3.08	8.44	270.5	2.85
Al_2O_3	15.60	3.01	20.1	15.23	12.03	4.70	39.9	10.15	8.84	5.64	64.1	6.77
Fe_2O_3	6.15	2.14	35.6	5.86	9.58	10.01	105.1	6.86	7.29	6.86	94.1	5.01
MgO	2.82	1.66	59.1	2.49	3.15	2.82	89.2	1.82	2.49	4.32	172.9	2.14
	n = 17				n = 8				n = 13			

For explanations see Table 22.

character of rocks, observable chiefly in slates of the Harmónia Group, caused by the expansion of organisms during volcanic activity. The supply of SiO_2 can be effected via exhalations and hydrothermal solutions into water environment, which may induce suitable conditions for carbonification of organic remains, and thus a larger amount of organic matter may accumulate in sediments.

Table 24

Basic statistical parameters of major elements in the examined samples of black slates, arranged according to grain-size and the grade of metamorphism

	Granularity								Metamorphism rank							
	Fine-grained				Medium-grained				Epi-				Meso- Kata-			
	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM
K_2O	1.44	1.20	81.0	1.15	1.20	1.44	115.1	1.04	1.44	1.56	105.8	1.20	1.20	1.03	93.9	1.12
SiO_2	61.85	12.20	19.7	60.35	54.14	16.26	29.9	48.58	54.57	16.48	30.4	48.15	59.49	11.98	20.2	53.21
Na_2O	1.74	1.47	87.2	1.43	2.81	5.09	173.6	2.23	2.68	5.89	218.1	2.43	2.55	1.47	60.9	2.34
Al_2O_3	9.96	5.08	52.0	8.46	12.78	5.26	41.6	10.71	11.28	5.26	44.7	9.44	12.97	5.07	39.3	11.47
Fe_2O_3	7.29	7.01	96.1	5.15	7.86	7.58	97.7	5.86	7.15	6.86	96.1	5.00	7.29	5.43	73.6	6.29
MgO	1.33	1.16	79.2	1.10	3.15	3.65	110.5	2.96	2.82	3.98	138.9	2.61	2.49	1.83	71.2	2.18
	n = 22				n = 59				n = 44				n = 37			

For explanations see Table 22.

Table 25

Basic statistical parameters of major elements in the examined samples of black slates arranged according to the content of sulphides and samples from the Pezinok—Pernek crystalline complex

	Sulphide content											
	Type A				Type B				Type C			
	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM
K_2O	1.32	1.32	100.0	1.13	1.08	1.32	112.9	0.94	0.24	0.36	123.4	0.19
SiO_2	58.42	12.41	21.4	56.71	57.35	17.55	30.7	47.29	34.24	17.98	52.4	30.60
Na_2O	2.41	1.34	59.7	1.74	3.88	8.57	214.3	3.32	0.54	0.40	71.9	0.40
Al_2O_3	13.54	4.52	32.3	12.59	10.53	5.64	54.6	8.46	1.88	0.94	49.9	1.63
Fe_2O_3	6.01	3.29	54.2	5.01	7.15	4.29	58.9	5.86	32.03	13.03	37.3	29.88
MgO	2.57	2.32	85.7	2.21	2.82	4.48	153.3	2.52	0.33	0.33	100.0	0.24
	n = 52				n = 20				n = 4			

	Pezinok — Pernek crystalline area											
	Productive zones as a whole				Productive zones type A				Productive zones type B + C			
	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM
K_2O	1.08	0.96	98.0	0.89	1.06	0.96	98.0	0.91	0.96	1.03	114.1	0.91
SiO_2	56.50	16.69	29.4	50.07	58.85	14.34	24.4	56.71	54.14	19.47	36.1	44.08
Na_2O	2.81	6.16	214.6	2.22	1.74	1.34	80.9	1.07	3.75	8.58	222.6	3.58
Al_2O_3	10.15	5.45	53.7	8.27	11.09	4.88	44.3	9.96	8.65	6.02	70.9	6.20
Fe_2O_3	8.86	7.01	79.3	7.01	7.29	3.72	50.7	6.43	11.44	10.29	90.4	8.01
MgO	2.98	3.65	121.9	2.53	3.15	2.49	82.1	2.32	2.49	4.48	175.1	2.06
	n = 39				n = 21				n = 18			

For explanations see Tables 18 and 22.

The relationship between the grain-size of rocks and the contents of SiO_2, Al_2O_3, MgO and Na_2O is seen from Table 24. A higher SiO_2 content in finer-grained varieties of slates has been confirmed by petrographical study, which revealed that quartz in black slates is predominantly fine-grained and slightly recrystallized. Metamorphism (Table 24) is responsible for the increase of SiO_2 and Al_2O_3 contents; the contents of other macroelements do not change perceptibly, which is connected with the reduction of organic matter and sulphides in higher metamorphosed schist types.

Table 26

Basic statistical parameters of major elements in the samples of black slates from the crystalline basement and in samples arranged on stratigraphic basis

	Subjacent crystalline area											
	Pezinok—Pernek crystalline area outside productive zones				Bratislava area				Modra—Orešany area			
	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM
K_2O	0.96	1.20	134.2	0.81	1.92	1.56	84.2	1.65	1.68	2.52	141.4	1.32
SiO_2	56.28	14.34	25.4	54.36	52.22	14.98	28.8	49.01	61.20	9.20	15.1	60.78
Na_2O	2.82	1.88	65.2	1.88	2.55	1.21	51.8	2.01	1.88	1.61	91.0	1.34
Al_2O_3	13.16	3.38	26.1	12.60	15.23	5.26	35.1	12.78	16.92	4.7	28.4	16.54
Fe_2O_3	4.43	3.29	72.6	3.15	9.29	11.15	119.0	6.72	4.29	1.14	28.2	4.14
MgO	2.49	2.65	102.9	2.16	2.32	1.16	53.5	1.34	1.49	0.99	65.9	1.33
	n = 11				n = 12				n = 2			

	Stratigraphy											
	Subjacent crystalline area as a whole				Harmónia Group				Younger formations (Triassic)			
	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM
K_2O	1.08	1.08	100.0	0.81	1.80	1.92	107.8	1.63	2.64	2.4	88.8	2.42
SiO_2	55.85	16.26	29.1	50.72	57.14	14.34	25.2	53.50	51.36	3.42	6.8	51.36
Na_2O	2.68	4.96	182.5	2.19	2.01	1.34	68.4	1.79	2.41	1.07	44.1	2.14
Al_2O_3	11.09	5.45	49.1	9.02	13.72	3.76	28.3	12.97	20.12	0.38	2.5	20.12
Fe_2O_3	8.44	8.15	96.0	6.15	4.72	2.00	45.0	4.15	8.01	2.57	32.7	7.72
MgO	2.66	3.32	120.4	2.45	3.15	3.98	122.3	2.32	3.49	1.00	29.6	3.32
	n = 64				n = 14				n = 3			

For explanations see Table 22.

An outstanding decrease in the content of essential elements (esp. Si and Al) results in the increase of ore elements, as is seen from Table 25. In type C (sulphide ore) the contents of SiO_2, Al_2O_3, K_2O, MgO and Na_2O are extraordinarily low, compared with type A (black slates devoid of sulphides). The high content of Fe_2O_3 (the value is of total Fe) is connected with the increased content of sulphidic minerals in the rock.

Certain relations between the content of macroelements in the black slates of the Malé Karpaty crystalline complex follow from the arrangement of rock samples on the regional and stratigraphic bases (Table 26). A higher SiO_2 con-

Table 27

Basic statistical parameters of major elements in the samples of black slates arranged according to mineralogy

	Silica visually								Biotite, garnet				Amphibole			
	more				less				feldspar							
	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM
K_2O	1.08	1.08	100.0	0.76	1.68	1.68	100.0	1.34	1.08	1.32	122.7	0.82	1.08	0.96	88.4	0.91
SiO_2	64.63	11.34	17.8	59.70	44.94	12.84	28.4	42.37	58.42	10.7	18.5	57.14	57.99	6.42	29.6	54.57
Na_2O	3.08	5.63	185.3	1.61	2.01	1.47	74.7	1.92	2.55	1.34	56.1	2.10	1.74	1.47	80.6	1.07
Al_2O_3	11.09	4.70	42.7	9.59	13.35	5.83	44.0	11.09	13.54	4.70	34.9	12.41	9.40	5.64	60.5	7.33
Fe_2O_3	5.43	3.57	65.3	4.29	10.53	9.87	92.8	8.01	6.43	5.00	79.3	5.29	10.44	10.58	101.6	7.44
MgO	2.01	2.99	153.6	1.82	3.82	3.15	84.7	3.48	2.49	1.66	70.7	2.06	2.16	2.16	100.0	1.94
	n = 46				n = 35				n = 36				n = 20			

For explanations see Table 22.

Table 28

Basic statistical parameters of major elements in the samples of black slates affected by hydrothermal alteration, mylonitization and weathering, and in samples having a higher content of carbonates

	Hydrothermal alterations				Mylonitization, weathering				Higher portion of carbonates			
	AM	AD	CV	GM	AM	AD	CV	GM	AM	AD	CV	GM
K_2O	0.84	0.84	100.0	0.71	1.92	1.44	73.2	1.74	1.80	1.20	69.9	0.96
SiO_2	52.86	19.47	36.8	49.01	59.71	7.70	12.8	59.28	41.10	15.84	38.8	37.45
Na_2O	2.41	1.34	54.6	2.01	2.01	1.74	83.6	1.07	1.21	0.94	83.4	0.81
Al_2O_3	12.60	3.76	30.0	12.03	13.91	4.13	30.2	13.35	11.66	5.45	47.2	9.78
Fe_2O_3	7.29	4.29	59.1	6.01	6.86	2.71	40.4	6.43	10.15	8.72	86.1	7.86
MgO	3.49	2.82	79.9	2.66	2.32	0.99	45.0	1.99	4.81	4.48	91.5	3.65
	n = 9				n = 9				n = 12			

For explanations see Table 22.

tent distinguished the slates from the Modra—Orešany area (a small number of samples must be taken into consideration) and the black slates of the Harmónia Group. A high content of Al_2O_3 (up to 20.12 %) is typical of shales of the younger formations.

The differences in the contents of macroelements in the rocks studied (Table 27) are caused by the differences in the representation of rock-forming minerals (given in the heading of the Table).

The contents of macroelements analysed in black slates affected by hydrothermal alteration, mylonitization, weathering and in slates having a higher proportion of carbonates are listed in Table 28.

It must be especially remarked that the results obtained by means of the INAA method using the generator have not been verified yet sufficiently by other analytical methods.

The comparison of the contents of essential macroelements in the individual sets reveals many cases of differences but these can be readily explained on petrological basis. It can be stated, however, that the division of macroelements into groups according to the above given criteria does not exhibit such conspicuous differences between the sets, as has been observed in microelements (trace elements). This is due to the fact that the contents of trace elements are not controlled to such a degree by the contents of essential elements forming the rock-forming minerals, but rather by elements that are characteristic of the black slates and are a product of particular genetic conditions of these slates. These factors involve the content of organic component in the rock and of sulphides, the grade of metamorphic recrystallization of the rock, and the intensity of additional alterations, which are decisive for the geochemical composition of slates, as concerns the content of microelements.

For illustration, in Table 29 containing complete chemical analyses of the

Table 29

Complete chemical analyses of black slates of the Malé Karpaty crystalline complex

Sample number	8 B	13 A	19 A	26 A	27 A	39 A	41 A	50 A	59 A	62 A
Fe_2O_3	7.10	2.26	2.57	6.70	1.18	8.54	5.85	7.35	4.78	11.77
MnO	0.19	0.02	0.05	0.10	0.15	0.11	0.01	0.09	0.10	0.06
TiO_2	1.03	0.48	0.69	1.04	1.74	1.19	0.47	0.74	0.58	0.37
CaO	3.31	1.11	5.64	2.58	10.37	2.40	0.26	29.52	2.52	4.61
K_2O	2.93	2.16	3.99	3.42	0.48	3.69	1.54	0.71	3.18	1.08
SiO_2	60.61	72.81	65.86	61.81	57.26	56.49	75.82	33.88	62.88	60.51
Al_2O_3	17.64	14.42	12.96	17.15	11.37	19.48	7.48	12.85	15.87	6.54
MgO	3.61	0.68	1.82	3.21	5.38	2.78	0.41	4.46	1.80	2.89
Na_2O	1.22	2.87	0.21	1.14	0.44	0.64	0.31	2.35	0.50	0.75
H_2O^-	0.16	0.16	0.25	0.29	0.32	0.14	0.27	0.08	0.05	0.27
H_2O^+	2.61	3.14	5.87	2.73	3.42	4.13	7.44	7.99	7.59	11.05
Σ	100.61	100.11	99.91	100.17	100.12	99.69	99.86	100.02	99.85	99.90
B	3	44	71	54	43	62	126	1	141	10
V	93	390	480	15	89	162	590	155	126	720
Cu	115	91	19	5	10	62	16	49	13	209
Ni	66	5	12	5	5	27	41	48	35	288
Co	14	1	3	3	1	3	3	26	14	19
Cr	93	35	295	5	37	115	87	49	57	60
Ba	780	12000	12000	12000	590	12000	200	930	690	470
Sr	182	174	123	32	174	390	30	251	91	49
Ti	5600	3200	6200	1860	6300	4800	2690	5750	4000	2690
Zr	57	186	148	110	269	126	139	69	132	190
C_{org}	1.13	1.23	5.02	0.18	—	0.18	2.84	0.01	—	4.90
Th	6.1	—	11.1	10.1	1.8	7.8	2.1	0.6	6.5	0.4
U	3.1	—	9.9	2.6	2.2	6.4	14.0	0.9	2.4	24.0

Explanations: macroelements (X-ray fluorescence anal., Geol. Inst. Slovak Acad. Sci., Bratislava — in %); trace elements (SPA Geol. Inst. of Comenius University, Bratislava — in g . t^{-1}); C_{org} (conductometry, Geol. Survey, branch, Brno — in %); Th, U (γ — spectrometry, Geol. Inst. Slovak Acad. Sci., Bratislava — in g . t^{-1}); — undetermined.

black slates of the Malé Karpaty crystalline complex, the silicate analyses are accompanied by the results of determinations of the trace elements.

This Table permits to study the relationships of micro- and macroelements, as shown by the analyses of samples of the black slates. SiO_2 varies within a wide range — from 75—82 to 33—87 %, Al_2O_3 from 17.14 to 6.54, MgO from 5.38 to 0.41 %, K_2O from 3.99 to 0.48 %, Na_2O from 2.87 to 0.21 %, CaO from 29.52 to 0.26 %, and Fe_2O_3 — 2.26 to 11.77 %. Accordingly, the loss by ignition ranges within 11.0—2.61. The Table confirms the lithological variability of the black slates, as recorded in the first paragraphs of Section II.8. The microelements have relatively stable high contents of Ba and Ti and approximately equal Zr contents. The amounts of other microelements vary considerably, their contents depending obviously on C_{org}, Fe and Ca. However, the contents of trace elements in many cases increase or decrease irrespective of mutual relations-

Table 30
Complete chemical analyses of metapelites of the Harmónia Group

	24 63-JV	11-C	KV-43 423 m	175 A	177 B	178 B	183 B	184 A	30 63-JV	53 63-JV	Average
SiO_2	65.52	67.96	69.61	55.73	65.72	64.93	52.34	60.25	68.24	71.96	64.26
TiO_2	0.77	0.63	0.65	1.03	0.78	0.86	0.98	0.93	0.65	0.63	0.79
Al_2O_3	15.50	12.69	13.89	18.25	16.29	15.53	17.96	16.17	11.59	11.16	14.90
Fe_2O_3	2.03	2.24	0.62	3.29	2.29	2.06	4.44	4.05	1.56	2.70	2.53
FeO	3.21	0.41	3.14	4.63	2.30	2.09	4.10	3.73	3.31	2.38	2.93
MnO	0.10	0.05	0.08	0.12	0.07	0.10	0.16	0.15	0.09	0.05	0.09
MgO	1.51	2.20	2.20	4.21	2.77	2.52	4.36	4.19	1.24	1.37	2.66
CaO	3.25	3.70	2.19	3.01	2.85	3.11	4.64	2.47	3.64	2.16	3.10
Na_2O	3.10	1.29	3.76	2.78	3.22	2.65	2.08	2.35	3.00	2.90	2.71
K_2O	2.25	3.66	2.08	3.32	2.14	3.08	3.80	3.07	2.50	2.22	2.81
H_2O^-	0.10	0.48	0.19	0.59	0.35	0.27	0.34	0.34	0.37	0.18	0.32
H_2O^+	1.27	4.77	1.14	2.59	1.30	2.94	4.69	2.26	3.77	2.26	2.70
Σ	98.61	100.08	99.55	99.55	100.08	100.14	99.89	99.96	100.08	100.09	99.80
Ga	63	—	14	22	16	16	27	24	28	11	22
Cr	—	85	48	82	63	64	78	74	65	51	61
V	153	302	72	158	111	100	160	119	66	71	131
Ni	100	< 3	17	44	23	18	53	37	22	16	33
Co	21	< 3	6	19	9	7	30	17	17	18	14
Cu	3	74	8	95	8	9	44	30	59	10	34
Zr	176	119	167	135	130	160	137	244	257	126	165
Sc	30	13	9	21	11	12	18	14	30	30	19
Pb	10	13	5	7	8	12	6	6	35	18	12
Sr	40	176	105	71	198	100	204	244	115	76	133
Ba	1230	3700	748	733	565	493	1187	1412	955	830	1185
Y	28	56	16	30	17	23	33	32	13	10	26
La	204	—	—	—	—	—	—	—	72	69	115
Be	—	< 3	—	—	—	—	—	—	—	—	3
B	—	62	44	23	31	42	28	35	—	—	38
Sn	—	6	—	—	—	—	—	—	—	—	6
Th	12.7	9.3	—	—	—	—	—	—	7.7	8.3	9.5
U	4.1	7.0	—	—	—	—	—	—	2.2	1.2	3.6

Explanations: Working numbers in the first line correspond to serial numbers in the catalogue: 24 63-JV = 202; 11 C = 203; KV-43/423 = 204; 175 A = 187; 177 B = 189; 178 B = 190; 183 B = 205; 184 A = 206; 30/63-JV = 207; 53/63-JV = 208.

Table 31

Complete chemical analyses of metamorphic rocks of the Malé Karpaty crystalline complex, arranged regionally

	Bratislava massif area		Modra massif area		Pezinok—Pernek crystalline area		Harmónia Group	
	Gneisses	Phyllites	Gneisses	Phyllites	Gneisses	Phyllites	Gneisses	Phyllites
SiO_2	61.87 36	62.96 13	64.87 1	66.97 6	65.42 14	60.22 16	—	62.77 9
TiO_2	0.89 36	0.87 13	0.79 1	0.74 6	0.80 14	0.91 16	—	0.82 9
Al_2O_3	17.39 36	16.74 13	16.50 1	13.28 6	15.42 14	16.51 16	—	15.80 9
Fe_2O_3	3.09 36	3.04 13	0.95 1	1.64 6	3.15 14	4.47 16	—	2.61 9
FeO	3.99 36	3.25 13	3.87 1	3.82 6	3.30 14	3.43 16	—	2.97 9
MnO	0.19 36	0.10 13	0.08 1	0.08 6	0.13 14	0.14 16	—	0.10 9
MgO	2.65 36	3.10 13	2.11 1	1.68 6	2.21 14	2.77 16	—	3.03 9
CaO	2.10 36	1.71 13	2.12 1	3.71 6	1.90 14	2.56 16	—	3.15 9
Na_2O	3.01 36	2.47 13	4.09 1	3.21 6	3.24 14	2.73 16	—	2.67 9
K_2O	2.76 36	3.03 13	2.52 1	2.27 6	2.32 14	2.53 16	—	2.88 9
H_2O^-	0.32 23	0.45 11	0.16 1	0.31 6	0.34 8	0.49 16	—	0.34 9
H_2O^+	1.40 36	2.64 13	1.36 1	2.31 6	1.48 14	3.13 16	—	2.58 9
Ga	39 5	15 3	51 1	26 6	21 1	27 11	—	25 8
Cr	101 37	94 14	—	60 6	97 14	83 16	—	65 10
V	139 37	116 14	102 1	87 6	133 14	138 16	—	142 10
Ni	58 37	64 14	38 1	27 6	43 14	84 16	—	38 10
Co	31 37	22 14	15 1	19 6	24 14	20 16	—	14 10
Cu	50 37	58 14	23 1	69 6	33 14	81 16	—	39 10
Zr	217 37	185 14	270 1	209 6	217 14	223 16	—	165 10
Sc	27 37	25 14	30 1	30 6	25 14	19 16	—	16 10
Pb	16 37	15 14	29 1	22 6	14 14	11 16	—	8 10
Sr	253 37	180 14	191 1	230 6	198 14	172 16	—	153 10
Ba	555 37	541 14	460 1	709 6	530 14	692 16	—	1152 10
Y	37 35	30 14	29 1	18 6	37 14	44 16	—	31 10
La	121 5	90 3	168 1	90 6	107 1	—	—	204 1
Be	3 32	2 11	—	—	2 13	3 5	—	3 2
B	18 32	57 11	—	—	20 13	38 14	—	38 10
Sn	15 32	14 11	—	—	10 13	8 5	—	7 2
Mo	<1 23	<1 9	—	—	<1 8	—	—	—
Th	8 14	7 5	12 1	8 6	7 6	7 7	—	10 3
U	5 14	5 5	3 1	2 6	4 6	4 7	—	5 3

Explanations: macroelements — contents in per cent; trace elements — contents in $g.t^{-1}$; — no record; numbers in denominators give the number of analytical data from which arithmetic mean was calculated.

hips. Table 29 is thus an example of lithological and geochemical variability of the black slates in the Malé Karpaty region.

The Harmónia Group is characterized by average complete silicate analyses and analyses of trace elements, compiled in Table 30. The results of silicate analyses display a greater equality of macro- and trace elements. From this it follows that this slate complex was deposited under fairly stable sedimentation conditions, and that their petrochemical and geochemical patterns can be more easily expressed even by single analyses. The sequence is characterized by a relatively high content of SiO_2, by approximately equal contents of K_2O

Table 32

Average content of Th, U, K and the Th U ratio in granitoids and clayey-siliceous divided on the basis of regional and radiometric data

Rock type		Bratislava massif area				Pezinok—Pernek crystalline area				Modra massif area			
		Th g.t^{-1}	U g.t^{-1}	K %	Th U	Th	U	K	Th U	Th	U	K	Th U
Leucocratic fine-grained microcline granite to granodiorite	$\bar{x}$	5.4	1.5	3.2	3.5								
	S	4.3	0.7	0.7	2.7								
	R_{min}	1.1	0.6	1.0	0.9								
	R_{max}	16.3	4.7	4.3	16.0								
	N	33											
Two-mica, medium-grained granite to granodiorite	$\bar{x}$	11.8	2.2	3.1	5.6								
	S	3.3	0.7	0.4	2.7								
	R_{min}	4.7	1.0	1.8	1.6								
	R_{max}	21.0	5.8	4.3	19.6								
	N	88											
Biotite granodiorite to tonalite	$\bar{x}$	12.5	2.0	2.6	6.5					8.3	1.7	2.2	5.3
	S	4.1	0.6	0.5	3.1					1.5	0.5	0.4	2.3
	R_{min}	6.7	1.1	1.4	2.4					4.6	0.7	0.7	2.2
	R_{max}	18.8	3.1	3.3	12.8					15.4	3.1	3.4	11.8
	N	13								40			
Gneisses	$\bar{x}$	8.3	2.3	2.5	3.9	8.7	2.4	1.9	3.7				
	S	1.2	0.7	0.5	1.3	1.2	0.6	0.5	1.3				
	R_{min}	5.7	0.7	1.5	1.3	7.5	1.6	1.3	2.3				
	R_{max}	10.2	4.4	4.5	10.9	10.7	3.2	2.6	6.2				
	N	20				7							
Black shales Type I	$\bar{x}$	6.2	4.2	2.0	2.3	0.7	2.0	0.5	1.1				
	S	2.4	2.7	0.9	1.6	0.4	1.9	0.5	1.4				
	R_{min}	1.4	1.7	0.1	0.1	0.3	0.2	0	0.1				
	R_{max}	9.2	9.7	3.4	4.6	1.8	6.4	2.0	4.1				
	N	10				10							

Black shales Type II	$\bar{x}$	3.4	8.9	1.8	0.5				
	S	1.6	3.8	1.6	0.5				
	R_{min}	1.0	2.2	0.2	0.1				
	R_{max}	7.4	14.6	7.2	2.1				
	N	17							
Black shales Type III	$\bar{x}$	1.7	20.5	0.8	0.1				
	S	1.7	3.6	0.8	0.4				
	R_{min}	0.3	15.7	0	0.1				
	R_{max}	5.3	25.7	2.8	0.2				
	N	10							
Black shales Type IV	$\bar{x}$	1.4	43.2	0.6	0.1				
	S	2.2	7.1	0.3	0.3				
	R_{min}	0.3	36.3	0	0.1				
	R_{max}	6.7	63.5	1.4	0.1				
	N	13							
Black shales Type V	$\bar{x}$	6.6	2.7	2.2	3.0	6.8	2.9	2.0	2.6
	S	0.8	1.2	1.1	2.9	0.8	0.9	0.7	1.3
	R_{min}	5.3	0.7	0.1	1.2	5.7	1.3	0.5	1.5
	R_{max}	7.9	6.4	4.5	13.0	8.0	4.2	2.9	5.4
	N	17				7			
Black shales Type VI	$\bar{x}$	9.3	2.5	2.5	4.1	10.6	5.2	3.2	2.5
	S	1.1	0.9	1.5	1.6	1.5	2.6	0.9	1.2
	R_{min}	8.1	1.5	0.5	2.8	8.6	2.6	1.7	1.1
	R_{max}	11.1	3.8	4.8	6.6	13.0	9.9	4.9	4.9
	N	5				13			

Contents of Th and U in $g.t^{-1}$ and of K in per cent (Cambel — Kátlovský — Khun, 1981).
Explanations: $\bar{x}$ — arithmetic mean; S — arithmetic standard deviation; R_{min} — minimal content; R_{max} — maximal content; N — number of samples.

and Na_2O, and a high Ba content with a relatively low content of Sr. These analyses are taken from the papers of authors that are mentioned in the introduction of part II, and the documentation of the samples is to be found at the end of the catalogue. These analyses have not been included in the statistical computer processing.

The average values of phyllites and gneisses grouped according to regional standpoints are presented in Table 31.

The analyses were made to assess the chemical composition of biotite phyllites and biotite gneisses that occur outside the areas in which the complexes of dark slates were examined. Most of these rocks have small contents of organic matter. The clayey-siliceous pelitic metamorphites of the schist series form the mantle into which the Variscan granitoids had intruded.

The average contents of the essential minerals are fairly similar, not excepting the rock samples from the Harmónia Group. The fact that no substantial differences exist between macroelement contents in gneisses and phyllites indicates stable sedimentary conditions. It also suggests that the periplutonic--contact metamorphism did not produce a substantial petrochemical and geochemical differentiation but rather a petrochemical rapprochement. This is at variance with the conditions in the black slates, where metamorphism caused migration, of some microelements, in particular.

II.11. Uranium and thorium

The investigations carried out in the Malé Karpaty crystalline complex (Cambel — Khun, 1979; Cambel — Strešk o — Mičuda, 1981; Khun, 1980) have confirmed that the black slates of the productive zones had gained specific geochemical properties, chiefly under the influence of submarine volcanism, which distinguish them from other dark slates of the Malé Karpaty. This assumption is corroborated by geochemical studies of uranium and thorium reported on in the present paper. Table 32 gives the principal statistical parameters for Th, U, K and the Th/U ratio, divided according to the regional classification, the lithological and petrographical groups and the γ-spectrometric data on U and Th contents. It is well seen that the contents of Th in the granitoids of the Bratislava massif increase with the basicity of the rocks, from 5.4 g . t^{-1} in leucocratic granitoids to 12.5 g . t^{-1} in biotite granodiorites. The U contents are comparatively stable, varying within the range of 1.5 to 2.2 g . t^{-1}. The evident difference in the Th contents in the group of biotite granodiorites may be accounted for by a different scope of the sets compared, but also by the more heterogeneous and more leucocratic character of the granitoid rocks of the Bratislava massif. There is a conspicuous similarity in the Th and U contents and the Th U ratios in the biotite granodiorites of the Modra massif and in gneisses, which can be regarded as one of proofs for the palingenetic origin of granites. The values of Th and U contents in black slates are considerably different, depending on whether they belong to the Harmónia Group or this basement, or whether they are a component of an ore-bearing zone or of a complex outside it. This difference is particularly well seen in Table 33. The individual rock types differentiated according to radiometric data on U and Th contents (Table 32) show specific radiometric features. The mineralized

Table 33

Summarizing table of average contents of Th, U, K and the Th/U ratios in the crystalline rocks of the Malé Karpaty

		Productive zones			Outside zones		Black shales together	Gneisses to phyllites	Granitoides N=242
		Type B+C	Type A	Together	Harmonia Group	Together			
		N=26	N=36	N=62	N=17	N=40	N=102	N=27	
Th	$\bar{x}$	3.58	3.07	3.23	9.20	7.66	4.98	8.4	9.1
	S	3.23	2.72	2.94	2.70	2.84	2.91	1.2	
	R_{min}	0.3	0.3	0.3	2.80	1.40	0.3	5.7	
	R_{max}	11.1	9.0	11.1	13.0	13.0	13.0	10.7	
U	$\bar{x}$	19.69	12.46	15.15	4.30	4.27	11.10	2.3	1.9
	S	17.0	15.16	16.23	2.19	2.56	9.87	0.7	
	R_{min}	2.8	0.2	0.2	1.3	1.3	0.2	0.7	
	R_{max}	49.5	63.5	63.5	8.7	10.8	63.5	4.4	
K	$\bar{x}$	1.28	1.10	1.18	2.79	2.68	1.77	2.4	3.0
	S	1.10	0.88	0.97	1.21	1.36	1.02	0.5	
	R_{min}	0.1	0.1	0.1	0.53	0.53	0.1	1.3	
	R_{max}	3.79	3.51	3.79	4.94	7.29	7.29	4.5	
Th/U	$\bar{x}$	0.87	1.35	1.15	2.59	2.42	1.63	3.9	4.8
	S	1.25	1.95	1.70	1.35	1.45	1.50	1.3	
	R_{min}	0.1	0.1	0.1	0.7	0.1	0.1	1.3	
	R_{max}	5.3	9.2	9.2	5.4	6.6	9.2	10.9	

For explanations see Table 32.

black slates and ores represent types III and IV with a high U content (20.5—43.2 g . t^{-1}) and a low Th content (1.4—1.7 g . t^{-1}). The black slates of the types V and VI of the Pezinok—Pernek and Modra areas can be easily discriminated according to these two radioactive elements. Whereas in the Pezinok—Pernek area (basement) the rock type with U contents of 2.7 g . t^{-1} and Th contents of 6.6 g . t^{-1} predominates, the type with average U content of 5.2 g . t^{-1} and Th content of 10.6 g . t^{-1} is prevalent in the Modra area (Harmónia Group).

Figures 14 and 15 show the frequency of U and Th contents arranged according to the individual rock types. The dependence on the lithology of rocks and the intensity of metamorphic and metallogenetic processes is clearly seen from these Figures. In the slates and gneisses of the Harmónia Group there are distinct correlation trends of Th and U to K_2O (Fig. 16). The dependence of the U content on the content of organic carbon and conversely, a negative relationship of Th is indicated in Fig. 17. This fact provide evidence that uranium is genetically associated with organic carbon, whereas thorium in black slates is rather dependent on diadochic relations to certain rock-forming minerals.

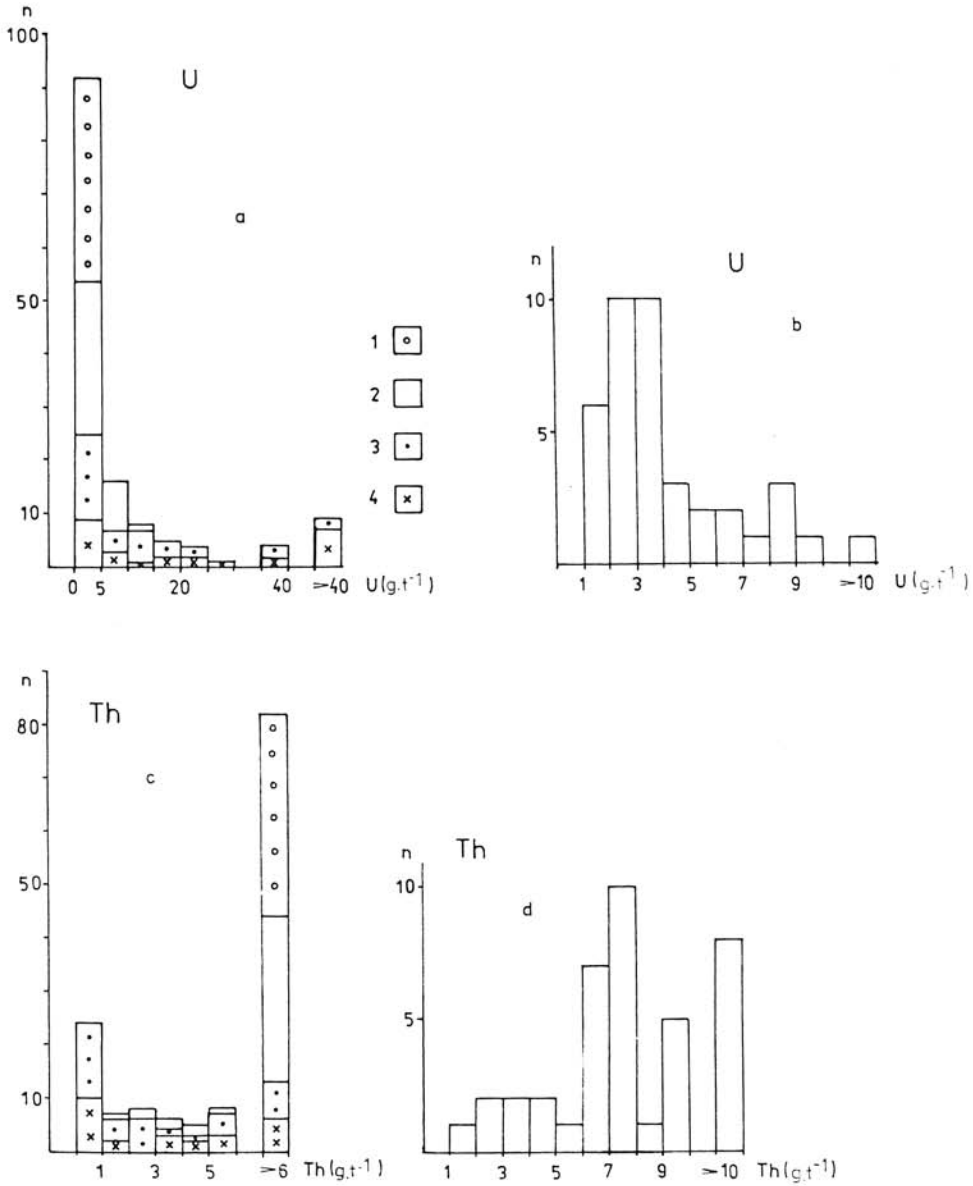


Fig. 14. Histograms of U and Th contents in various schistose rocks and ores of the Malé Karpaty Mts.

Explanations: Contents in g . t^{-1}; a, c — collective histograms; b, d — histograms of U, Th contents in black slates outside the productive zones; 1 — gneisses to micaschist phyllites; 2 — slates outside productive zones; 3 — black slates of the productive zones, type A; 4 — black slates of productive zones, type B and C (Cambel — Kâtlovský — Khun, 1981).

chiefly accessory minerals of the rocks studied. The two elements, even if accumulated in the same rocks, are controlled by diverse factors. The relative variability of rocks of the productive zones, depending on the variation of lithogenetic factors that are active in the course of the volcano-sedimentary process is depicted in Fig. 18, in which the rather broad boundaries of the field for these rocks attest to this variability.

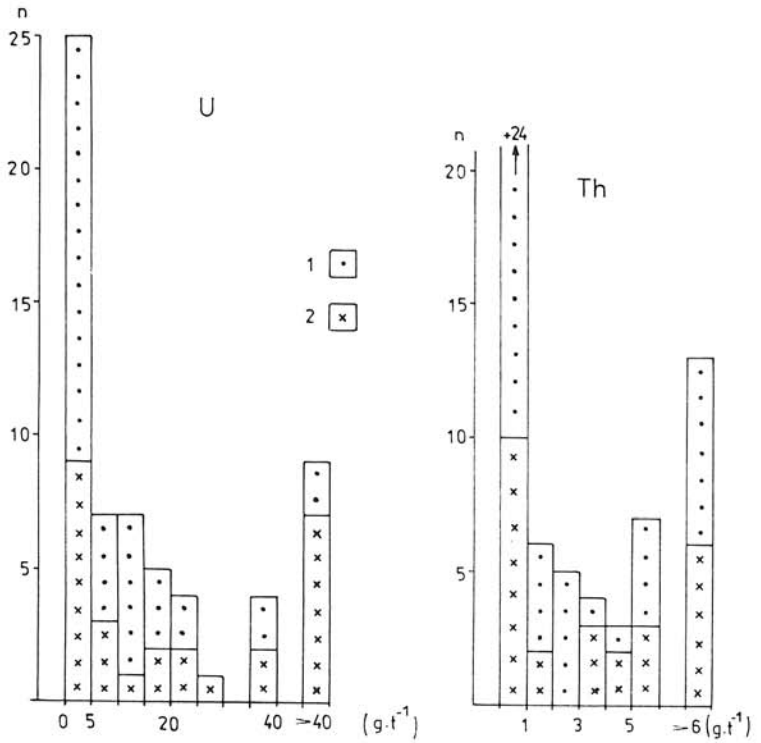


Fig. 15. Collective histograms of U and Th contents in black slates (type A) and in ores (types B, C) of the productive zones.
Explanations: 1 — rock type A; 2 — rock types B and C (C a m b e l — K á t l o v s k ý — K h u n, 1981).

It can be stated that the black slates of the productive zones have primarily increased U contents (Tables 33 and 34); their individual types have been discriminated and characterized according to the contents of this element. A peculiar geochemical pattern of the Harmónia slates allows an easy identification of them on the basis of the U, Th and K_2O contents and the Th/U ratio. It appears that the metamorphic process leads to a certain stable ratio of Th and U contents (Table 33), perceptible in gneisses and hybrid granitoids. The black slates do not attain this stabilized ratio, because the primarily increased U contents are bound to the organic component. The investigation of uranium and thorium in the sediments of the Malé Karpaty crystalline

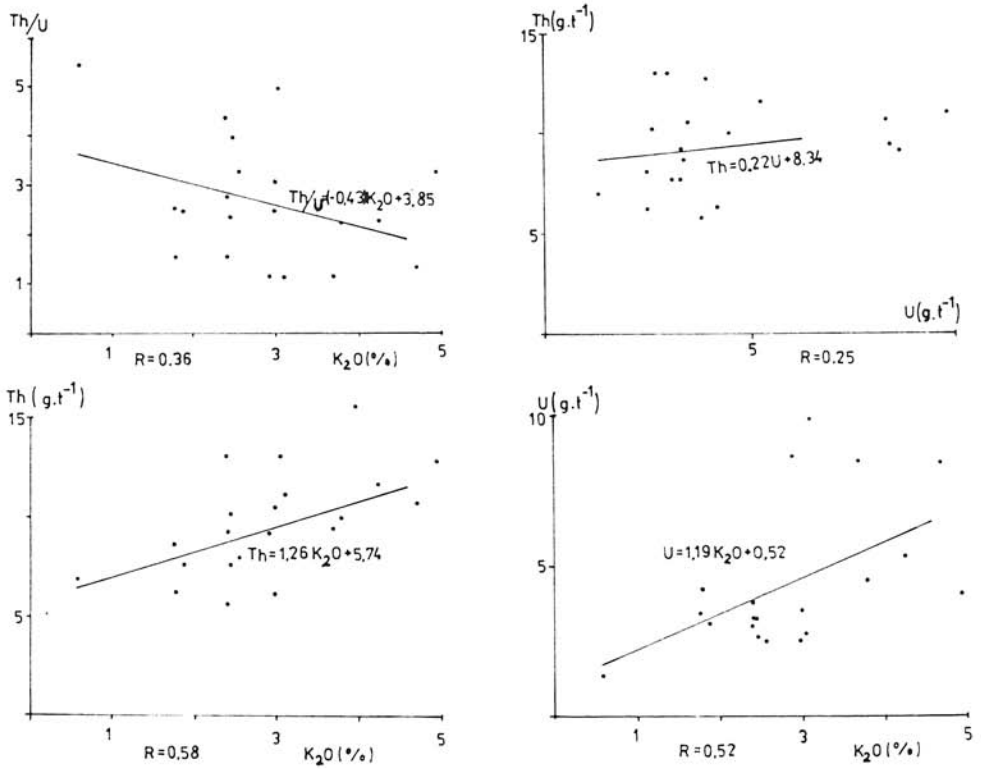


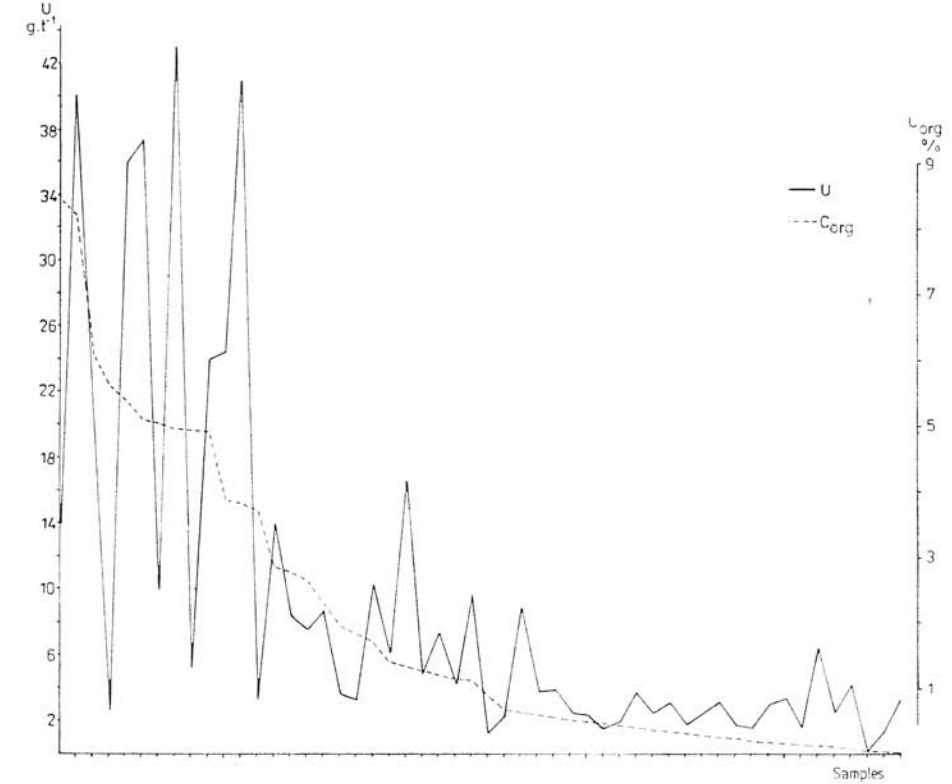
Fig. 16. Correlations of U, Th, Th/U and K_2O in black slates of the Harmónia Group (type according to radiometric data). R — correlation coefficient (Cambel — Kátlovský — Khun, 1981).

complex shows that useful genetic interpretation of the studied rocks, minerals and ores can be inferred from their results.

II.12. Interpretations and conclusions concerning the principal questions discussed in Chapter II

The study of elements, identified by means of spectral analysis (B, V, Cu, Ni, Co, Cr, Ba, Sr, Ti), and of the C_{org} contents, as well as the visual or microscopical estimates of the contents of pyrite, sulphides and other minerals, have confirmed that the establishment of rock sample populations, on the basis of

Fig. 17 a, b. Graph showing the relationship between C_{org} content and the contents of U and Th.
Explanations: U and Th contents in $g.t^{-1}$ — solid line; C_{org} content in % — dashed line. The samples are arranged according to descending C content.


U
g.t⁻¹
42
38
34
30
26
22
18
14
10
6
2
Corg
%
9
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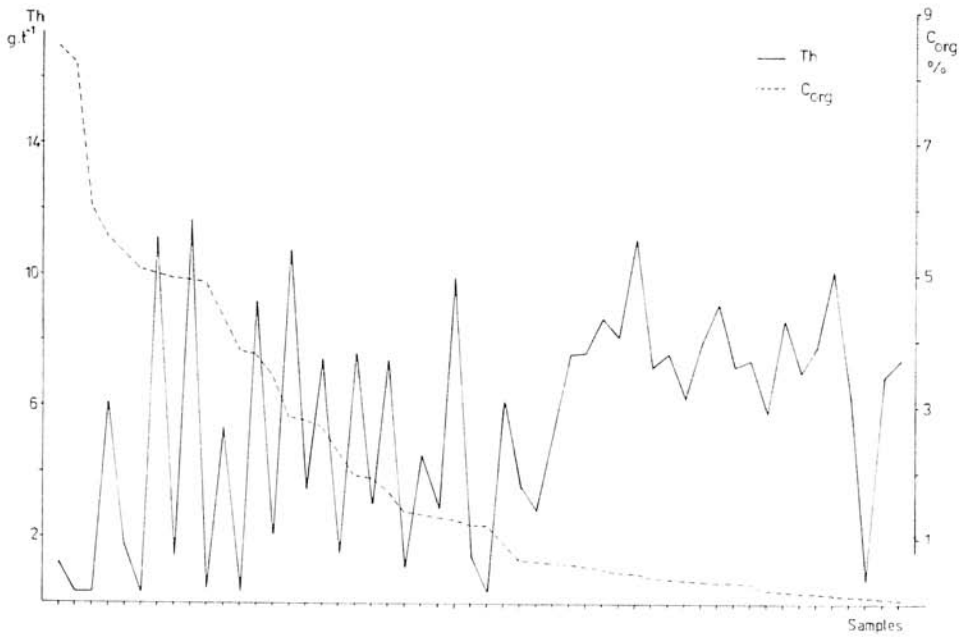
5
3
1
U
Corg
Samples


Th
g.t⁻¹
14
10
6
2
g
Corg
%
7
5
3
1
Th
Corg
Samples

the principles applied, makes it possible to draw conclusions usable in geochemical and lithological considerations. It provides appropriate geochemical and lithological means for the discrimination of rocks and a basis for petrological and metallogenetic, stratigraphic and regional-geochemical evaluation.

The most appropriate for geochemical and lithological interpretations appear to be the sets classified according to the C_{org} contents vs. sets showing a higher grade of metamorphism and a decreased C_{org} content, between which the contrast in geochemistry is the greatest. The sets of rock samples with visual contents of pyrite (B, C) and those devoid of pyrite (A) also display considerably contrasts. The geochemical peculiarity of the Harmónia Group (low contents of vanadium and strontium, high barium and titanium, and relatively stable U/Th ratio) is well demonstrated. The rocks of the productive zones in the underlying Pezinok—Pernek crystalline complex definitely differ from the slates outside the zones, chiefly in the increased

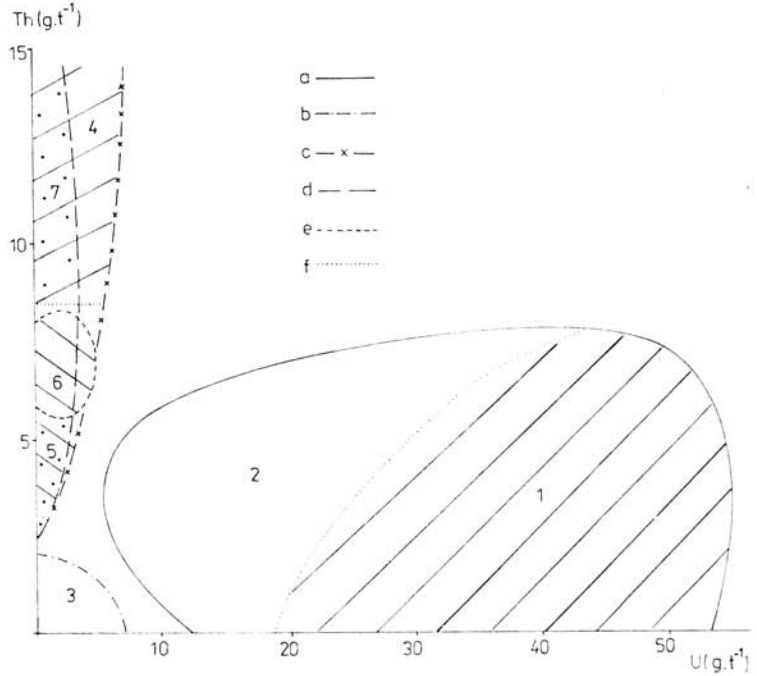


Fig. 18. Correlation graph of Th and U contents in the rocks of the Malé Karpaty crystalline complex.

Explanations: a — black slates and ores of productive zones; b — actinolite slates; c — black slates outside productive zones; d — granitoids; e — gneisses and micaschist-phyllites; f — boundaries dividing the fields into minor units differentiated by hachure. Rock types of the individual fields: 1 — mineralized slates to ores; 2 — black slates of the productive zones without visible mineralization; 3 — actinolite shales and metatuffs; 4 — black slates of the Harmónia Group; 5 — black slates outside productive zones; 6 — gneisses and micaschist-phyllites; 7 — granites.

contents of metals of the polymetallic group, of elements of the Fe group, of uranium, barium, vanadium and organic carbon, and in the decreased strontium. Geochemical differences of the rock sets based on mineral contents are most striking between the amphibole-bearing rocks and the clayey-siliceous metamorphites with biotite, garnet and feldspars. The metatuffites, compared with metapelites, have higher contents of boron, vanadium, copper, nickel, C_{org} and decreased strontium, titanium and zirconium contents. The group with an increased content of carbonates resembles in geochemistry the group of rocks altered hydrothermally or tectono-metamorphically. As concerns the content of microelements, there are no substantial differences between the two last-named groups.

From the values given in Table 6, which presents the average analyses of black shales from other regions, it can be inferred that the black slates of the Malé Karpaty crystalline complex, taken as a whole, are relative to an average black shale in the sense of V i n e and T o u r t e l o t (1970), enriched mainly in V, Cu and Ni and can be termed, in accord with these authors as the "metal-rich black slates". As concerns the contents of some trace elements (V, Cu, Ni, Cr and Sr) these slates are similar, for example, to the underlying sulphidic graphitic phyllites of the Chvaletice deposit.

The determination of the conditions under which the black slates of the Malé Karpaty crystalline complex were generated is a difficult problem to solve unequivocally and definitively for the very reason that the investigations are still under way. It should be remarked that the conditions of the origin of the Malé Karpaty black shales were changing in space and time. Thus, for example, in the Early Palaeozoic (beginning already in Late Proterozoic) geosynclinal stage with a distinctly detrital sedimentation in a relatively shallow sea, they had to be differing from those under which the dark slates of the Harmónia Group originated (Devonian, Lower Carboniferous). In the pre-Variscan geosyncline, special conditions also existed in the different parts of the crystalline basement, as e.g. where the productive ore-bearing complexes were forming. These developed in the subsiding and fault zones which were influenced by submarine volcanism.

For the origin of the black shales in the productive zones we could put forward a generalized conception of a deepening elongated sea basin, representing a longitudinal mobile zone extending at right angles to the present-day course of the Malé Karpaty Mts. This partial tectonic basinal structure with active basic volcanism was a site of a greater supply of metallic elements into the sediments and of an increased carbonification of organic matter. Volcanism was of pulsative character and repeated several times, probably in two principal and a few subordinate phases. During every phase there was an interval of big effusions of basic magma, followed by intervals of minor effusions connected with intensive exhalations (CO_2, H_2O, SO_2, halogenides) and ejections of pyroclastics. The sediments of this period represent the productive ore-bearing zones with pyrite deposits and abundant black shales having an increased amount of metals of the polymetallic group. To explain the formation of black slates of the productive zones we may apply the model described by D i d y k et al. (1978). It presumes limited circulation in silled basins and submarine tectonic depressions suitable for the accumulation of sediments rich in organic matter. The relevant point of this model is that the content of

oxygen present in water is not renewed by circulation so that the accumulation of sediments rich in organic substances may occur even at a relatively small organic production. As is seen, a type of euxinic environment is concerned, which is represented, for example, by the Black Sea or a sea basin with a fjord topography in submarine environment.

The conditions were evidently different when the black shales of the Harmónia Group were deposited during the interval of the Devonian — Early Carboniferous. In that case a shallower marine environment of a continental shelf or a neritic environment may be considered, in which the generation of black shales is common (Petránek, 1963). The sea floor was not in rest, and the alternating sediments, detrital and pelitic, were deposited intermittently with pyroclastic intercalations and minor local extrusions of basaltoids with a porous structure. Besides, lenses and layers of carbonates of organogenic derivation were formed. This model of a less reducing environment for the accumulation of black shales was already suggested by Krauskopf (1976).

The differences between the two environments studied are also indicated by a different geochemical and lithological character of black slates in the underlying crystalline complex and in the Harmónia Group. Further data are necessary for a more detailed knowledge of these environments.

III. Group of polymetallic elements in productive zones of the Malé Karpaty, and the genesis of deposits

The investigation of the genesis of the Malé Karpaty ore deposits, carried out by integrated geochemical study of the rocks of the crystalline complex, have provided geochemical characteristic of black (dark) slates, which are the fundamental rock type of the ore-bearing zones and contain sulphide and antimonite deposits. The results of the geochemical studies of black slates were compared with the geochemistry of dark slates occurring outside the ore-bearing zones. The dark slates of the Harmónia Group (Devonian to Lower Carboniferous) belong in this group. This comparison has demonstrated to what extent the rocks of the productive zones in the Pezinok—Pernek crystalline complex are enriched in metallic elements in relation to black slates outside the productive zones and/or to slates of the Harmónia Group. It has also shown whether they can be regarded as primary accumulators of metals of the group Cu, Sb, Hg, Au, Pb and Zn. From this point of view, the increased contents of Sb in slates of the productive zones are of primary importance for the determination of the potential primary source of this element.

In order to obtain information about the mode of occurrence of the above-mentioned metals in ore minerals and ores, analyses were performed on pyrite-bearing slates and sulphide ores, divided into a heavy and a light fraction. It should also be ascertained on which fraction the metal elements are bound, whether on the silicate or carbonaceous (light) fraction or the ore (heavy) fraction. The two fractions were obtained by gravity separation of detritus of the rock samples in water current on a separation table (Chapter II).

An interesting procedure was used for the determination of the relationship between the elements of polymetallic ores and other elements and the amount of organic matter in rocks and ores.

The chemical-analytical studies of the metals were performed by means of different procedures, in many cases on the same samples, so as to attest the reliability of the individual methods, or identical rock samples were analysed using the same method in different laboratories. The investigations were carried out by several analysts and geochemists of the Department of Geochemistry and Geological Institute of the Faculty of Sciences of Comenius University,

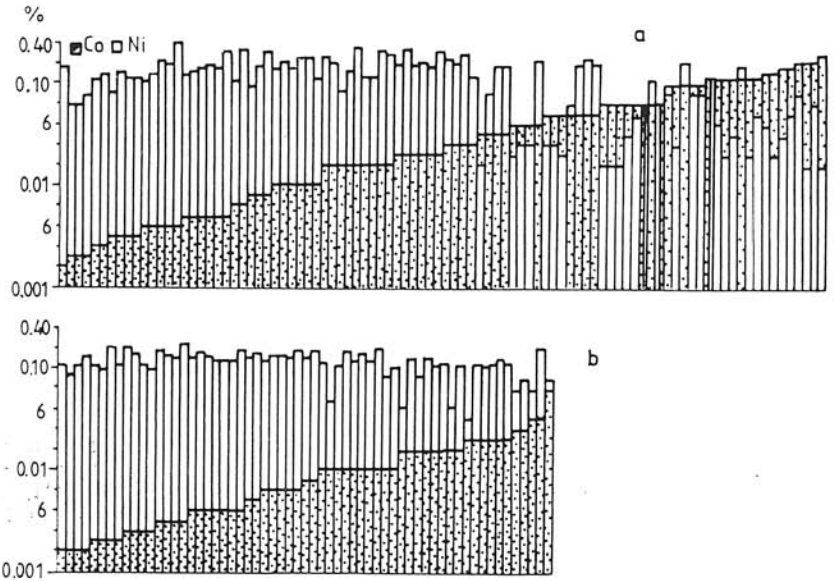


Fig. 19 a. Pyrite of higher metamorphosed ores containing pyrrhotite. The lower content of nickel than that of cobalt in pyrite has been found only in pyrrhotite-bearing ores.
Fig. 19 b. Pyrites of sulphide ores of nearly identical grade of metamorphism (carbonaceous quartz-sulphide ores without pyrrhotite). 1 — content of nickel; 2 — content of cobalt. Cambel — Jarkovský (1976).

and of the Geological Institute of the Slovak Academy of Sciences. As mentioned in the paper of Cambel — Streško — Škerenčáková (1980) gold analyses and their results were compared with the results of analyses of the same samples analysed in the Institute of Geochemistry, Acad. Sci. U.S.S.R. in Irkutsk and the IGEM Institute in Moscow (Sb, Hg).

Valuable results in the investigation of sulphur and carbon isotopes were obtained thanks to the cooperation with the laboratory of the D. Štúr Geological Institute (Kantor's papers of 1972—1974) and with the Institute of Geology and Physics of Minerals in Kiev (IGFM Acad. Sci. U.S.S.R. — Žukov — Savčenko in Cambel — Žukov — Savčenko, 1981).

The conclusions of the investigations into the genesis of pyrite ores of the

stratiform type and of epigenetic antimonite deposits occurring in association with the sulphide formation, are based on the following arguments:

The sulphides of the two deposit types exhibit an evident geochemical difference, which is caused by different conditions controlling the endogenic and exogenic metallogenetic accumulation processes.

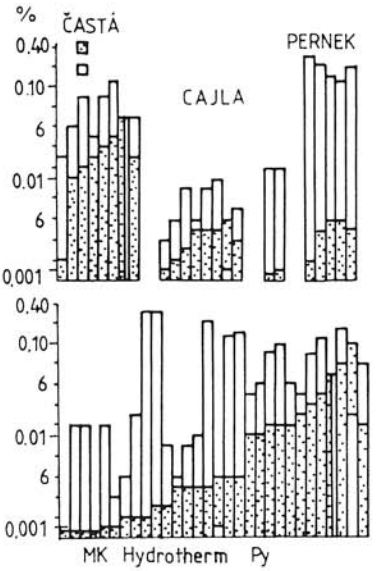


Fig. 20. Unequal contents of Ni and Co in pyrites of hydrothermal Sb mineralization in the Malé Karpaty. Deposits: Pernek, Pezinok, Cajla, Častá. Cambel — Jarkovský (1976).

The geochemical differences between the minerals of the sulphide formation (especially pyrite and pyrrhotite) and the antimonite mineralization have been discussed in the papers of Cambel — Jarkovský (1967, 1969). The evidence for these differences is provided by the graphs. Figures 19 and 20 confirm the different distribution of Ni and Co in syngenetic and epigenetic pyrites accompanying the Sb mineralization. The equal contents of Ni and Co in pyrites corroborates their syngenetic origin (stable P-T conditions at their origin) and, in contrast, the unequal contents suggest an origin influenced by superimposed plutogenic processes changing in time, viz. by the recurrent changes of hydrothermal solutions. Metamorphic recrystallization of sulphide ores (Fig. 19 b) induces under certain thermodynamic conditions the formation of pyrrhotite and migration of Ni into its lattice. This results in the reduction of Ni in pyrite below the level of Co, the content of which increases.

Of particular metallogenetic significance is the determination of gold in pyrites from the hydrothermal ores accompanying the antimonite accumulations (Figs. 21, 22) and in pyrites of the sulphide formation. These investigations have been carried out by Cambel — Strešk o — Škerenčáková (1980) and their results are complemented in the paper of Cambel — Strešk o — Mičuda (1981). According to the results obtained, the content of gold in hydrothermal pyrites is more than 100 times higher than in syngenetic pyrites.

(The gold contents in syngenetic pyrites are of the order of thousandths g . t^{-1}, and in hydrothermal pyrites they are of the order of tenths g . t^{-1}). The investigations of gold contents in the pyrites of syngenetic derivation have shown differences even in this category, which are caused by both primary and

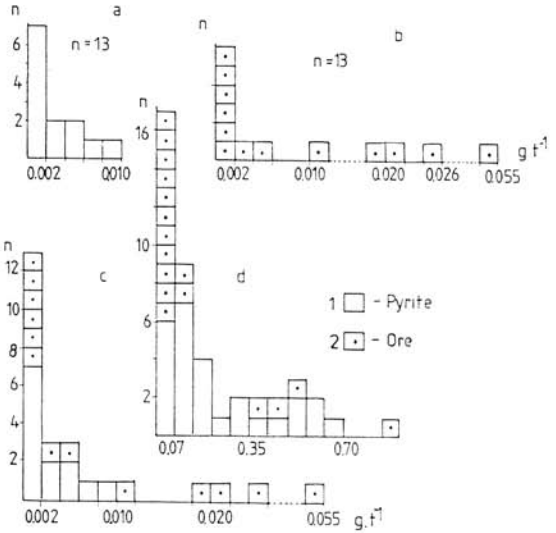


Fig. 21. Histograms of gold contents in the pyrites of syngenetic ores and ores of hydrothermal Sb mineralization in the Malé Karpaty Mts.

Explanations: 1 — contents of gold in pyrite; 2 — contents of gold in samples of ores from which pyrite was separated. Histograms a, b -pyrite and syngenetic ores; c — summation histogram (a+b); 4 — summation histogram of gold contents in the West Carpathian hydrothermal deposits (Cambel — Streško — Škerenčáková, 1980).

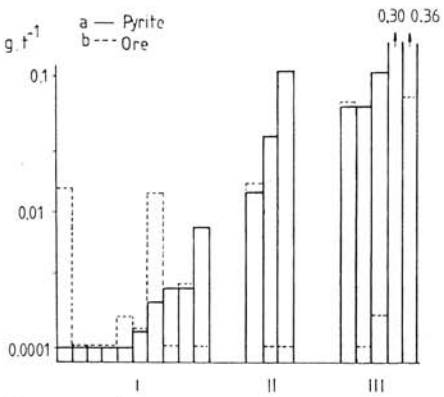


Fig. 22. Contents of gold (in g . t^{-1}) in pyrites and samples of the Malé Karpaty ores from which pyrites were separated.

Explanations: a — pyrite; b — original sample; I — syngenetic pyrite; II — pyrite affected by metamorphism; III — hydrothermal pyrite. (Cambel — Streško — Škerenčáková, 1980).

Table 34 a

Contents of Sb, Hg, Zn, Cu and Au in black slates and ores of the pyrite formation within the „productive" sequence of the Malé Karpaty Mts. crystalline

Sample number	Sb			Hg		Zn	Cu		Au
	INAA	AAS	MAS	AAS	CH	AAS	AAS	SPA	INAA
	III	I	IV	I	IV	I	I	I	III
7 B	—	31.5	—	0.29	—	53	105	159	—
9 B	—	52.4	—	0.19	—	32	40	81	—
12 A	—	—	—	0.18	—	197	165	525+	—
13 A	—	11.2	—	0.18	—	27	62	91	—
15 A	—	—	—	0.68	—	270	128	239+	—
16 A	—	305.0+	—	0.31	—	30	20	8.3	—
33 A	—	12.0	—	1.75+	—	30	78	95.5	—
34 A	—	45.0	—	1.62+	—	40	66	110.0	—
35 A	—	6.0	—	0.25	—	555+	114	170	—
40 B	26.60	230.0+	—	0.74	—	180	44	53	<0.004
41 A	13.30	67.2	60.0	0.70	0.20	105	23	16	0.012
42 B	22.00	—	40.0	0.62	0.20	60	73	93	<0.004
43 C	35.50	—	—	0.75	—	225	88	176	<0.005
44 A	52.50	307.0+	—	0.17	—	70	54	79	0.035
45 A	0.50	3.2	1.6	0.17	0.02	105	91	130	0.005
46 A	12.40	41.6	—	0.70	0.9	65	72	115	0.011
47 C	—	—	—	0.60	—	210	121	186	—
48 B	3.30	10.0	—	0.52	—	247	169	257+	0.031
49 A	0.82	4.4	6.0	0.17	0.02	212	98	103	0.004
50 A	125.00	1080.0+	—	0.18	0.02	70	93	49	0.145+
51 A	—	1033.0+	—	0.23	0.04	140	33	22	—
52 B	10.70	51.0	—	0.30	—	150	100	166	<0.006
53 B	4.50	23.0	—	0.65	—	60	67	60	0.025
54 A	—	10.0	12.0	0.46	0.09	89	77	46	—
55 C	3.70	28.0	—	1.14	—	665+	410+	415+	0.023
56 A	—	1.9	—	0.50	0.30	30	28	24.5	—
57 A	6.15	30.4	—	0.18	0.02	55	78	66	<0.004
58 A	3.30	14.4	16.0	0.13	0.02	120	46	10	<0.005
59 A	24.70	97.6+	80.0	0.38	0.04	92	126	13	0.008

60 A	38.50	254.5+	200.0	0.18	0.07	151	65	159	0.136+
61 A	—	3.8	—	0.18	—	475+	159	234+	—
62 A	48.00	259.8+	—	0.27	—	80	155	209+	0.029
64 A	—	—	—	0.60	—	385+	23	—	—
66 A	—	23.0	—	0.23	—	40	57	—	—
67 A	28.00	240.0+	300.0+	0.32	0.08	302	152	234+	<0.005
68 A	18.60	80.0	—	0.18	0.02	110	65	36	0.427+
69 A	—	47.0	—	0.18	—	74	40	30	—
70 B	15.40	80.0	—	0.60	—	110	52	15.5	0.029
71 C	25.50	172.0+	—	0.30	—	512+	360+	25.5	0.023
82 B	0.53	6.4	—	0.45	—	168	30	43	<0.004
84 B	156.00	0.5	—	0.44	—	94	16	16.2	<0.008
97 A	43.00	160.0+	—	0.35	—	50	85	20	0.380+
98 A	1.55	10.0	—	0.40	—	20	16	20	0.040
99 A	7.15	40.0	—	0.37	—	700+	234	191	0.002
100 B	0.69	7.0	—	0.57	—	85	84	115	<0.005
102 A	0.84	7.0	—	0.45	—	1000+	25	14.1	0.010
104 A	0.40	2.0	—	0.27	—	65	73	85	<0.005
108 A	—	6.0	—	0.35	—	35	16	4.8	—
124 B	—	34.8	50.0	0.22	0.06	540+	126	263+	—
137 B	—	2.0	2.5	0.17	0.05	146	128	117	—
157 B	—	2.8	1.0	0.42	0.09	66	286+	12.6	—
X*	—	23.4 34	26.9 10	0.39 49	0.03 18	106.1 43	80.4 48	80.2 41	0.299 4
X	24.3 30	109.7 45	64.1 12	0.44 51	0.08 18	184.2 51	96.4 51	110.3 49	0.013 26

Explanations: INAA — neutron activation analysis; AAS — atomic absorption spectrometry; SPA — spectrochemical analysis. Values are in $g \cdot t^{-1}$ (p.p.m.); MAS — molecular absorption spectrometry (Ozerova, IGEM, Moscow); Ch — chemical methods (idem). Samples A — black slate without visible sulphide content; B — mineralized black slate with visible pyrite content; C — pyrite and pyrite-pyrrhotite ore of syngenetic origin. Numbers in denominator indicate number of analyses in the set. Numbers with crosses are considered anomalous and these are not included into computations of the arithmetic mean. Such average values are indicated by asterisk (X^*). Average values without asterisk (X) are computed from all values of the sample set. Limits for elimination of anomalous values are for data obtained by AAS as follows: Sb — 80, Hg — 1.0, Zn — 300, Cu — 200 $g \cdot t^{-1}$. For values obtained by INAA: Sb — 350, Hg — 0.1 $g \cdot t^{-1}$. Limit of determinability (LD) is 0.01 $g \cdot t^{-1}$; — not analyzed. Laboratories and their indication in tables: I — Geological Institute of the Comenius University, Bratislava (GÚ UK); II — Geological Institute of the Slovak Academy of Sciences, Bratislava (GÚ SAV); III — Central Laboratories of the Czechoslovak Uranium Industry, Stráž pod Ralskem (ÚL ČSUP); IV — Institute of Geology of Ore Deposit, Petrography, Mineralogy and Geochemistry, Moscow (IGEM); V — Geochemical Institute, Siberian Branch of the Academy of Sciences USSR, Irkutsk.

Table 34 b

Contents of antimony, mercury, zinc, copper and gold in black slates of the Malé Karpaty Mts. outside productive zones belts (slates of the Harmónia Group including

Sample number	Sb			Hg		Zn	Cu		Au
	INAA	AAS	MAS	AAS	CH	AAS	AAS	SPA	INAA
	III	I	IV	I	IV	I	I	I	III
17 A	0.11	—	—	0.80	—	135	236+	330+	<0.004
18 A	—	0.7	—	0.25	—	105	37	37	—
19 A	0.49	1.1	—	0.25	—	50	26	19.5	0.022
20 A	—	0.5	—	0.30	—	100	26	25.1	—
21 A	—	1.7	—	0.26	—	40	20	7.4	—
22 A	—	1.3	—	0.25	—	45	20	12.3	—
23 A	—	4.4	—	0.52	—	280	30	18.2	—
24 A	—	0.8	—	0.18	—	90	42	35	—
25 A	—	2.3	—	0.20	—	90	88	104	—
26 A	—	0.9	—	0.30	—	55	20	5.4	—
92 A	0.68	—	—	0.12	—	150	133	65	0.013
94 A	0.34	—	—	0.16	—	100	28	11.5	0.014
107 A	0.21	1.7	—	0.23	—	125	42	16.6	<0.004
110 A	0.15	1.2	—	0.40	—	55	24	33	<0.005
111 A	0.59	1.4	1.0	0.25	0.05	86	30	44	<0.005
112 A	1.10	3.7	—	0.17	0.11	100	7	10.4	<0.004
113 A	0.22	2.0	—	0.30	0.12	80	6	9.1	<0.006
114 A	0.17	0.5	2.5	0.27	—	10	24	50	0.005
121 A	3.65	0.8	—	0.18	0.06	132	20	22.9	0.020
128 A	0.92	3.0	—	0.23	0.03	108	154	195	0.019
138 A	—	9.8	—	0.30	—	132	21	21.9	—
147 A	—	2.3	1.6	0.44	0.05	140	14	28.8	—
156 A	0.37	1.4	0.8	0.25	0.02	58	20	14.5	0.009
161 B	—	0.5	0.6	0.50	0.02	72	11	3	—
162 B	0.07	1.0	0.8	0.22	0.04	28	12	5.1	0.009
163 A		0.9	0.6	0.33	0.02	32	12	11.5	
X*	—	—	—	—	—	—	34.7 25	32.2 25	0.005 14
X	0.65 14	1.9 23	1.1 7	0.29 26	0.05 10	92.2 26	42.4 26	43.7 27	0.009 14

Explanations as in Table 34 a.

secondary factors. For example, pyrite concretions and pyrites forming metamorphic filling of veinlets in primary sulphide ores have gold contents by one order of magnitude higher. From these results it can be inferred that the gold contents increase by about one order of magnitude at the remobilization of sulphides. The research has also shown that the gold contents can be applied, similarly as the contents of Ni and Co, to the study of genetic conditions of the pyrite aggregates here discussed, viz. their primary genetic particularities and the additional secondary influencing as well. The data on the contents of gold in ores and rocks of the Malé Karpaty Mts. are summarized in Table 34.

The investigation of sulphur isotopes in Sb-sulphides and in pyrites of diffe-

rent types of sulphide ores has also furnished interesting results; see K a n t o r (1972, 1974), Ž u k o v in C a m b e l — Ž u k o v — S a v č e n k o (1981).

Figures 23 and 24 show the differences of $\delta^{34}S$ ‰ values in the individual ore types. The hydrothermal minerals of Sb-mineralization have $\delta^{34}S$ ‰ values from 0 to —5 ‰, similarly as pyrites separated from the granitoids of the Malé Karpaty Mts. (average per-mil. deviation — δ 2.6 ‰). Another sulphide group

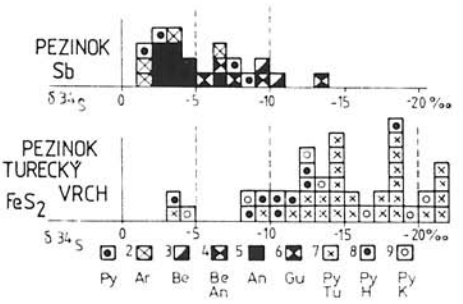


Fig. 23. Histogram of $\delta^{34}S$ ‰ in pyrite and Sb minerals. Upper part: minerals from the antimonite deposit Pezinok. Lower part: syngenetic pyrite from the Turecký vrch deposit.
Explanations: 1 — pyrite; 2 — arsenopyrite; 3 — berthierite; 4 — berthierite+antimonite; 5 — antimonite; 6 — gudmundite; 7 — pyrite from Turecký vrch; 8 — pyrite from the pit heap of the antimonite mine; 9 — pyrite from other places of the productive zone (K a n t o r, 1974 b).

of $\delta^{34}S$ ‰ has the values between —5 and —10. These belong to sulphides containing Sb and Fe, in which the isotopic composition is presumably a result of contamination of plutonic sulphur with exogenic sulphur. We have observed this phenomenon mainly in berthierite, gudmundite and pyrites, which form veinlets and epigenetic impregnations in rocks and older pyrite ores of the sulphide formation, where $\delta^{34}S$ ‰ values range from —5 to —10. The deviation

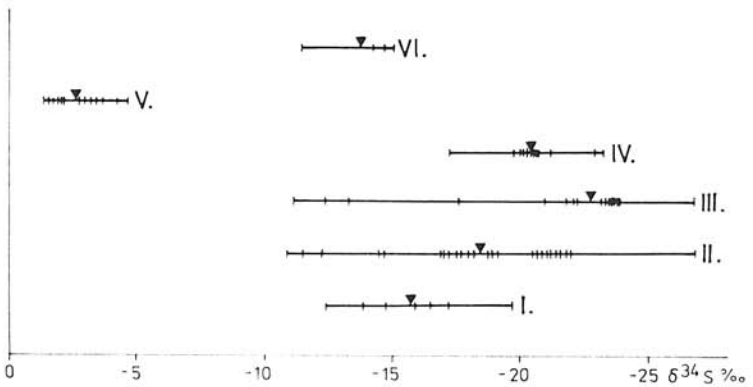


Fig. 24. Graph showing the percentage values of δ^{34} S ‰ from various types of pyrite ore of the sulphide formation — the belt of deposits, Augustín-Čmele (Malé Karpaty).
Explanations: I — disseminated pyrite in black slates and metapelites (X — 15.9); II — high-carbonaceous pyrite ores and/or mineralized black slates (X — —18.7); III — recrystallized siliceous-sulphide and amphibole-sulphide ores with a minor content of C component (X — —22.9); IV — massive and compact pyrite and pyrite-pyrrhotite ores (X — —20.7); V — pyrite of the Malé Karpaty granitoids (X — —2.6); VI — pyrite of amphibolic metatuffites and amphibolites (X — —13.9) (Ž u k o v — S a v č e n k o in C a m b e l — Ž u k o v — S a v č e n k o, 1980).

Table 34 c

Contents of zinc, copper and mercury in pyrite

Locality	Sample number	Au					
		PH			TP	LP	Pyrites
		AAS I.	AAS V.	INAA III.	INAA III.	AAS V.	AAS I.
Karol horná	40 B	0.001	0.0055	<0.004	0.008	0.0090	0.001
Karol dolná	42 B	0.003	0.0022	<0.004	0.015	0.0015	0.001
Karol dolná	43 C	0.002	0.0014	<0.005	0.010	0.0090	0.002
Ján III.	47 C	0.001	0.0067	0.036	0.037	0.0030	0.001
Ján III.	48 B	0.001	0.0065	0.031	0.027	0.0104	—
Pernek	52 B	0.021	0.0147	<0.006	0.026	0.0145	0.004
Augustín horná	53 B	—	0.0075	0.025	0.034	0.0052	—
Augustín horná	55 C	0.001	0.0022	0.023	0.026	0.0056	0.001
Kolársky vrch	70 B	—	0.0062	0.029	0.350	0.0930	—
Kolársky vrch	71 C	—	0.0090	0.023	0.029	0.0024	—
	X+	0.0043	0.0062	0.019	0.056	0.0164	0.002

Explanations: Analyzed light and heavy fraction and original rock. PH — original 42—B, 53—B, 70—B, — black slate with pyrite, 43—C, 47—C, 55—C — pyrite ore.

values of $\delta^{34}S$ ‰ between —10 and —28 are typical of syngenetic pyrites or other sulphides strongly influenced by bacterial activity during their genesis. As is evident from Fig. 25, the average values of $\delta^{34}S$ ‰ differ depending on the type of ore. Of interest is the consistent value of $\delta^{34}S$ ‰ in pyrites from the granitoids and Sb-sulphides (especially antimonite), which attests to an endogenic, i.e. volcanogenic origin of sulphur in these sulphides. The pyrites in granitoids may be of accessory origin or they may represent impregnations that were generated during the subsequent metamorphic or hydrothermal activity.

The causes of the differences in the isotopic composition of sulphur in Sb-sulphides and in pyrite from the granitoid rocks as compared with the pyrites of the sulphide formation cannot be explained unambiguously. The heavier sulphur in antimonites can be regarded as a plutonic sulphur that was not contaminated by bacterial activities, whereas the sulphur combined with iron in pyrites was affected by the action of bacteria. The comparison of the contents of economically important metallic elements in black slates of the productive zones with the dark slates outside these zones has shown that the elements Ni, Cu and V are increasingly cumulated in the slates of the mineralized zones

ores (C) and mineralized black slates (B)

Sb		Zn			Cu			Hg		
PH	ŤP	PH	ŤP	ĽP	PH	ŤP	ĽP	PH	ŤP	ĽP
INAA III.	INAA III.	AAS	AAS	AAS	AAS	AAS	AAS	AAS	AAS	AAS
26.60	11.00		165	30	44	80	32	0.74	0.71	0.80
22.00	11.70	60	40	26	73	73	72	0.62	0.60	0.70
35.50	5.80	225	170	160	88	88	80	0.75	0.70	0.78
5.40	4.15	210	135	120	121	136	85	0.80	0.71	0.97
3.30	2.57	247	82	70	169	180	159	0.52	0.44	0.60
10.70	12.90	130	150	130	80	191	80	0.34	0.25	0.34
4.50	4.15	60	30	25	67	67	33	0.67	0.60	0.75
3.70	3.15	665	385	545	410	430	250	1.14	1.60	1.25
15.40	515.00	100	160	87	52	100	31	0.60	0.17	0.60
25.50	2.82	512	432	422	360	410	400	0.30	0.30	0.45
15.26	56.32	238,9	174,9	161.5	146,4	175,5	122,2	0.65	0.55	0.72

rock; ŤP — heavy fraction; ĽP — light fraction. Characteristics of samples: 40—B, 71—C, 77—B, 78—B — quartz-sulphidic ore.

(Fig. 25). Discriminant analysis performed by K h u n (in C a m b e l — K h u n, 1979) and K h u n (1980) on these microelements has evidenced that from their increased contents and the Sb content it is possible to determine with much certainty (80 %) whether or not the rock examined belongs to the productive zone (i.e. to a complex with potential ore accumulations).

The distribution of Cu, Hg, Sb and Zn in the Malé Karpaty dark slates is evident from Figs. 26 and 27. They show that the dark slates of productive zones contain such increased amounts of Sb and Zn that they can be regarded as a potential source of these elements. During subsequent metallogenetic processes, especially under the influence of hydrothermal solutions, the metals (Sb, Pb, Zn) may then have been mobilized into present-day deposits. These facts are inferrable from Tables 35 and 36.

Figure 28 indicates a positive relationship between the contents of Cr, V and Ni and the carbon content in rocks. Such a relationship has not been established for copper. The increase in Ni content is connected with the increasing amount of pyrite in dark slates, as it is a carrier of nickel.

From Table 35 it is evident which elements cumulate in ores and slates in and outside the productive zones, or in heavy and light fractions of ores. These findings are also represented in graphs 29 and 30. Table 36 lists the

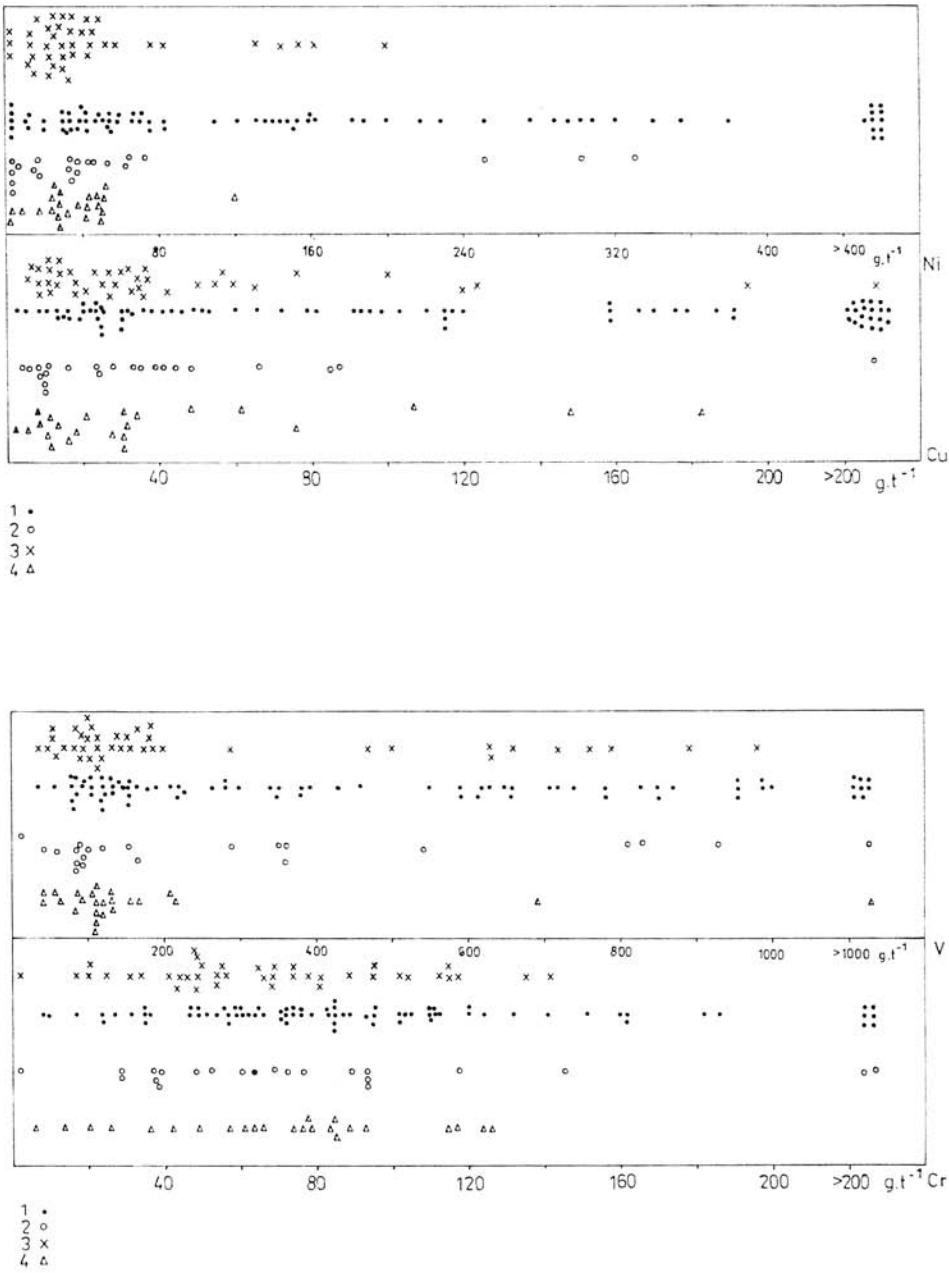


Fig. 25 a, b. Graph showing the contents of Ni, Cu, V and Cr (in g . t^{-1}) in the samples of black slates.

Explanations: 1 — productive zones; 2 — black slates outside the zones; 3 — Harmónia Group; 4 — Bratislava area.

average contents of Sb, Cu, Pb, and Ni in the rocks of the Malé Karpaty crystalline complex.

Table 36 reveals that the contents of Sb and Cu increase from granitoids through gneisses, phyllites to basic rocks. With some exceptions, the contents of these elements in metasediments increase in those rock types that were less recrystallized — in the order — gneiss, biotite phyllite, dark slate.

This fact corroborates the assumption that in a metamorphic process the elements Sb, Zn, Cu and others migrate from the rocks affected by a higher metamorphic recrystallization into zones showing a smaller recrystallization effect. This phenomenon may also account for the occurrence of Sb deposits in the productive dark slates, relatively low recrystallized, with varying contents of pyrite or carbon component. Tables 35 and 36 and graphs 29 and 30 throw light on the position of metallic elements in the analysed samples of ores separated on a gravity shaking table into a heavy and a light fraction (see also Fig. 2). It can be stated that except for Ni, Cu and Zr all elements present (Hg, Sb, Ba, Cr, Pb) have increased contents in the light fractions. On the

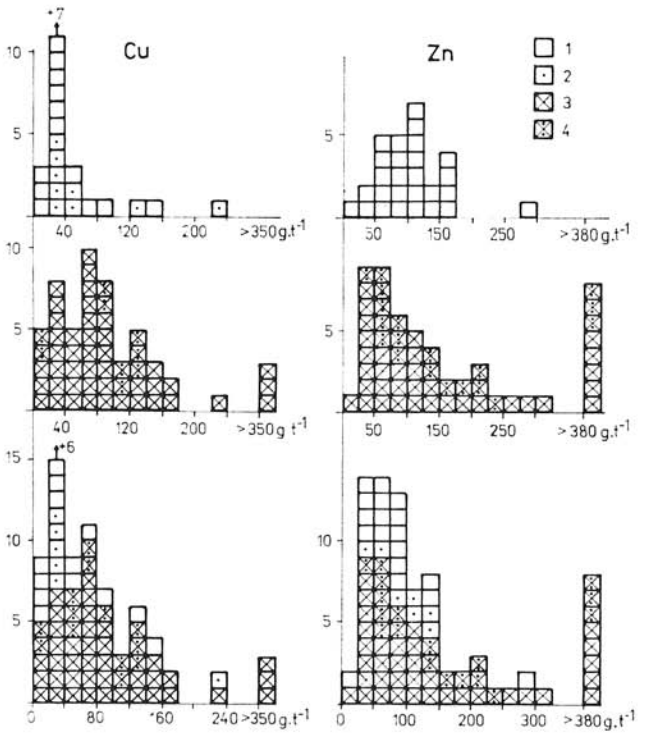


Fig. 26. Histogram of Cu and Zn contents (in g . t^{-1}) determined by the AAS method in black slates of the Malé Karpaty crystalline complex.

Explanations: 1 — black slates outside the ore-bearing zones; 2 — black slates of the Harmónia Group (Upper Devonian, Lower Carboniferous); 3 — black slates from productive zones; 4 — mineralized slates and pyrite ores of sulphide formation (Cambel — Streško — Mićuda, 1981).

basis of these data, however, we cannot decide reliably to what extent they are caused by the applied method of dividing the ores into fractions, and to what extent they result from the binding of the elements on the light silicate or carbonaceous mineral components in the form of a sorbent and fine dispersion or as the isomorphic component of silicate minerals. (This concerns mainly Pb, Ba and V). Antimony and mercury form obviously a dispersed component in dark slates, which is not concentrated into major aggregates in sulphidic minerals. The same holds for gold in rocks and sulphides (Table 34).

IV. Evaluation of data on the element contents obtained by neutron activation analysis

In Chapter IV the authors endeavour to determine the contents of rare earths (TR, REE) and other elements that could not be analysed by methods they had at disposal. With the application of neutron activation analysis, some elements were examined using two to three methods.

This part was aimed at demonstrating the differences in results obtained by different analytical methods. As the possibility to discuss the differences in

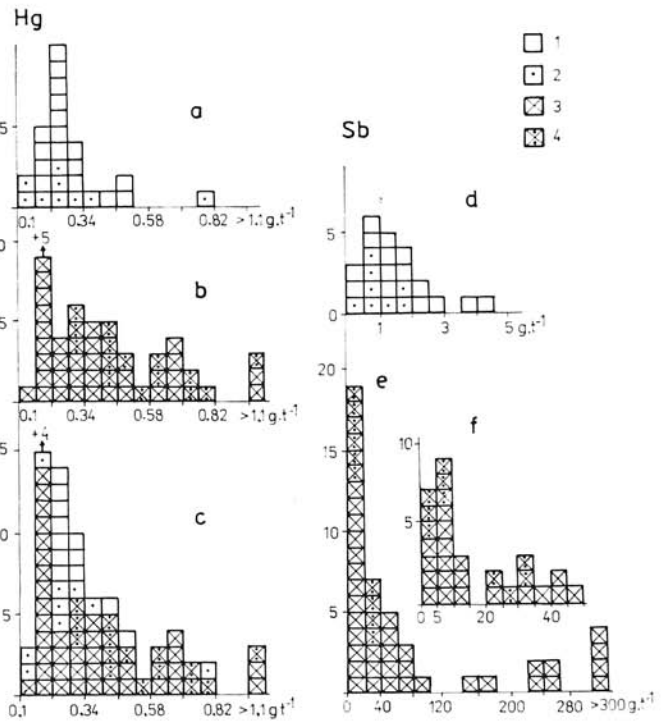


Fig. 27. Histogram of Hg and Sb contents (in g . t^{-1}). Histogram "f" represents evaluated analytical data within a range of 0—40 g . t^{-1}, classified according to decreased interval. (C a m b e l — S t r e š k o — M i č u d a, 1981). Other explanations as in Fig. 26.

Table 35

Average contents of elements Sb, Cu, Pb, Zn and Hg in black shales of the Malé Karpaty crystalline complex

		Productive zones					Outside zones	Together
		A,B,C	A	B,C	TP	LP	A	
Sb INAA	III.	30.2 46	27.9 31	34.9 15	57.0 10	—	0.7 18	26.64 74
Sb AAS	I.	23.6 34	22.6 21	25.3 13	—	—	1.5 23	16.14 58
Cu SPA	I.	90.7 36	97.0 27	72.2 9	143.1 6	89.6 7	41.6 38	65.5 74
Cu AAS	I.	76.0 47	72.8 32	82.9 15	175.5 10	122.2 10	36.6 25	62.4 72
Pb SPA	I.	14.5 43	11.3 29	21.1 14	16.0 10	18.6 10	4.9 38	9.99 81
Zn AAS	I.	102.74 42	90.3 27	125.1 15	174.9 10	161.5 10	86.9 26	97.7 68
Hg AAS	I.	0.40 41	0.32 29	0.56	0.50 9	0.67 9	0.30 15	0.37 56

Numbers in denominator give the numbers of analyses. LP — light fraction: TP — heavy fraction; — not analysed.
Further explanations as in Table 34 a.

Table 36

Average contents of Sb, Cu, Pb and Ni in magmatic and metamorphosed rocks of the Malé Karpaty crystalline complex (Cambel — Streško — Mičuda, 1981)

		Granites		Gneisses	Phyllites	Amphibolites
		Two-mica	Biotitic			
Sb INAA	III.	0.55 33	0.39 20	0.8 7	1.99 12	1.74 12
Cu SPA	II.	5.5 26	11.1 18	63.6 7	71.0 12	72.0 10
Pb SPA	II.	23.3 26	21.5 18	18.6 7	20.9 12	18.9 21
Ni SPA	II.	2.9 26	6.6 18	58.7 7	43.7 11	143.0 70+

Explanations: Contents in $g.t^{-1}$. Averages are computed from the analysed sets of samples studied by prof. B. Cambel, DrSc., Doc. RNDr. J. Veselský, CSc., RNDr. M. Dyda, CSc. and RNDr. J. Spišiak, CSc. Analysts: RNDr. J. Medveď, CSc. (GÚ SAV) — SPA analysis; Ing. P. Kotas, CSc. (ÚL ČSUP) — INAA. Numbers with crosses are taken from the paper of Cambel — Kupčo (1965). For other explanations see Table 34 a.

results was very limited, the data on some elements are only of informative character.

The interpretation of analytical results is given mainly in parts II and III, and is based on the following analyses: atomic absorption, spectrochemical, spectrophotometric and γ-ray spectrophotometric. The neutron activation ana-

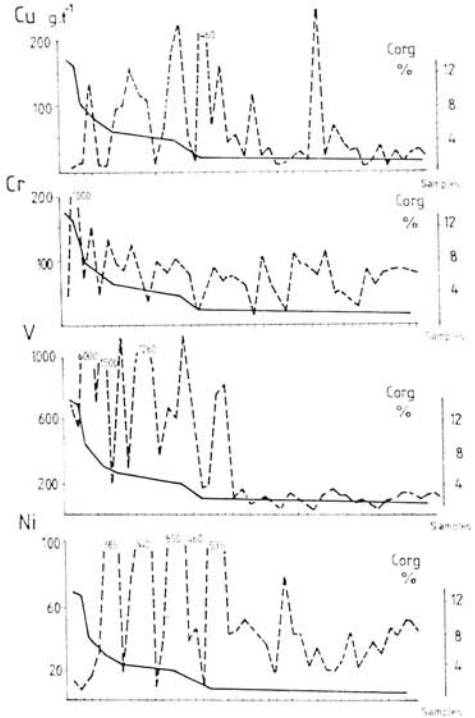


Fig. 28. Relationship between the contents of Cu, Cr, V and Ni and the content of organic carbon in rocks and ores.

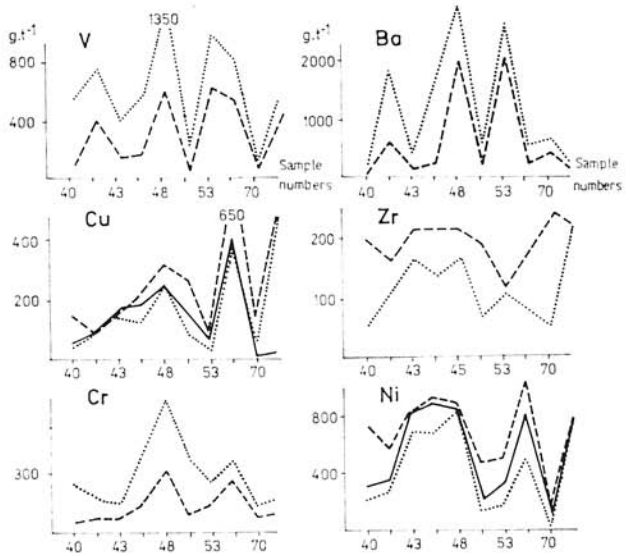


Fig. 29. Contents of V, Cu, Cr, Ba, Zr and Ni in heavy (TP) and light (LP) fractions of ores, and original samples (PH) with sulphide content (types B and C). Analyses made by SPA method. The contents of individual samples are arranged on x axis by chance.

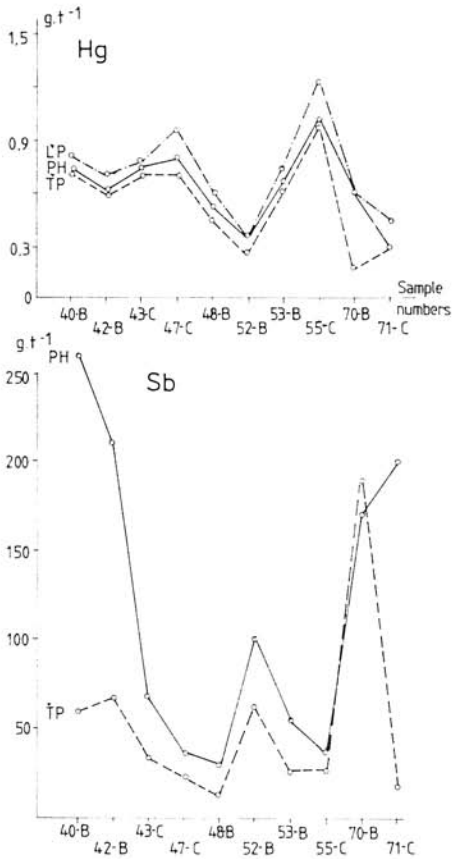


Fig. 30. Contents of Hg and Sb in heavy (TP) and light (LP) fractions and in original rock samples (PH). Analysis of Sb made by INAA method. (Cambel — Střeško — Mičuda, 1981.)

lysis was used for the determination of rare eaths elements (REE), Ta, W, Hf, Sc, Ga, As, which were not analysed by other methods and of some elements already examined by other analyses (Rb, Cs, Zn, Sb, U, Th and Au). This made it possible to compare the results, as the same samples were analysed by different methods and some of them in different laboratories. Neutron activation analysis of some elements gave results widely differing from those obtained by other procedures so that some values were even incomparable. Nevertheless, we present here the data on element contents obtained by neutron activation method, as it is not always clear which methods are most appropriate for individual elements (e.g. the As contents). At the present time, the correlation and verification studies are in the centre of our attention.

IV.1. Procedure of neutron activation analysis

The analyses were made in the Central laboratories of the Czechoslovak Uranium Industry (ÚL ČSUP) in Stráž pod Ralskem, at the Department of Radiometric Methods (head Ing. P. Kotas, CSc.).

Table 37 a

Table of trace element contents compiled by the means of INAA in ÚL ČSUP, Stráž pod Ralskem

Sample number	La	Ce	Sm	Eu	Tb	Yb	Lu	ΣREE	Th	U
41 A	21.0	32.8	5.4	1.2	0.7	3.1	0.5	62.0	3.2	5.9
44 A	18.7	47.2	5.0	1.3	0.6	1.8	0.4	72.5	6.3	0.4
46 A	35.6	27.9	7.0	1.3	0.8	3.8	0.6	73.5	0.9	3.5
58 A	13.2	43.6	1.2	1.0	0.6	1.5	0.2	60.7	6.6	<0.4
59 A	26.2	55.3	5.6	0.9	0.5	1.6	0.3	87.5	7.6	2.1
60 A	20.0	43.2	6.2	1.4	0.8	2.7	0.5	71.7	4.9	10.5
62 A	14.5	30.1	6.2	0.8	0.8	3.3	0.6	53.2	3.0	18.6
67 A	13.8	27.4	4.0	1.4	0.8	2.6	0.5	48.5	2.4	4.7
68 A	31.4	75.1	9.8	1.9	0.9	4.4	0.9	119.5	10.1	7.0
97 A	36.2	45.4	9.0	2.3	1.5	7.9	1.2	99.0	1.9	7.3
99 A	20.8	39.1	10.0	2.1	1.1	6.1	0.7	74.9	2.6	22.2
102 A	22.2	57.6	3.6	1.5	0.6	2.1	0.3	86.1	10.4	<0.3
54 A	18.2	23.4	4.4	0.9	0.4	2.3	0.4	47.8	1.2	4.1
61 A	19.6	41.4	7.0	1.8	0.9	4.5	0.8	72.5	4.0	30.4
164 A	17.8	20.9	7.0	1.4	1.1	3.7	0.7	49.1	3.2	8.3
166 A	20.4	11.2	7.6	1.7	1.1	4.1	0.8	43.1	1.6	6.6
167 A	12.0	13.7	2.0	0.9	0.7	3.0	0.6	31.9	4.6	8.9
168 A	13.4	11.3	5.0	1.7	1.1	3.8	0.7	34.5	0.4	3.7
170 A	17.8	12.3	5.0	0.8	0.5	2.8	0.4	37.1	3.1	19.3
171 A	15.2	20.5	5.6	1.0	0.7	3.5	0.7	44.4	4.2	6.0
173 A	14.2	15.1	4.6	0.8	0.6	2.7	0.4	36.1	2.3	9.5
174 A	14.8	12.8	5.0	0.9	0.7	3.8	0.8	36.3	3.0	19.7
$\bar{x}$ (22 sampl.)	19.8	32.1	5.6	1.6	0.8	3.8	0.7	61.6	3.9	9.1
45 A	1.8	79.2	0.8	1.1	0.4	1.5	0.2	84.6	<0.3	<0.3
49 A	6.0	9.4	3.0	0.9	0.3	1.5	0.2	19.8	0.5	3.3
50 A	1.2	33.7	0.4	1.3	0.1	1.4	0.1	38.0	<0.5	<0.5
57 A	8.4	14.4	3.4	0.6	0.4	1.5	0.3	27.3	5.8	7.7
94 A	8.1	14.4	1.8	0.3	0.1	0.7	0.1	24.6	7.6	7.3
98 A	2.6	7.4	2.8	0.3	0.3	1.5	0.3	13.8	1.3	7.0
100 A	1.4	5.7	0.4	1.2	0.2	1.9	0.4	11.0	0.4	<0.3
104 A	2.3	10.3	1.4	1.1	1.0	1.1	0.3	16.8	13.0	2.0
172 A	6.4	9.2	1.2	0.4	0.2	1.1	0.2	23.5	2.6	1.9
$\bar{x}$ (9 sampl.)	4.1	20.4	1.8	0.8	0.3	1.4	0.2	28.10	3.6	3.4
$\bar{x}$ (31 sampl.)	15.20	28.7	4.4	1.4	0.6	3.1	0.5	51.7	3.8	7.4

Slates of A type from the productive zones of the Malé Karpaty Mts. In the table a separate set with anomalously low La and Ce contents (9 samples) is distinguished. Numbers with asterisks are considered for anomalous values and they have not been included into the arithmetic mean. Mean without anomalous values is indicated X^+. Element contents are in g . t^{-1}.

Weights of 150—200 mg of homogenized samples of analytical fineness (< 0.061 mm) were pelleted and sealed in circular polyethylene casings (∅ 25 mm) wrapped in aluminium foil. The samples thus prepared were together with multielement standards (Řanda et al., 1978) and monitors of

Table 37 b

Table of trace element contents compiled by the means of INAA in ÚL ČSUP, Stráž pod Ralskem

Sample number	Au	As	Sb	W	Ta	Hf	Sc	Ga	Rb	Cs	Ag	Zn
41 A	0.012	84.5	13.30	1.9	0.3	2.9	11.3	13.4	80	2.4	<1.0	99
44 A	0.035	71.0	52.50*	1.6	0.9	3.9	33.0	16.0	188	3.3	<1.8	130
46 A	0.011	115.0	12.40	0.5	0.2	2.5	12.8	6.2	22	0.4	<1.2	65
58 A	<0.005	6.3	3.30	<0.4	0.5	5.0	19.2	<4.6	73	<0.4	<1.3	103
59 A	0.028	130.0*	24.70	7.4*	0.4	4.1	24.2	28.6	198	0.6	<1.5	41
60 A	0.136*	605.0*	38.50	4.6*	<0.2	3.5	18.2	16.2	64	0.6	<1.4	168
62 A	0.029	109.0	48.00*	5.8*	<0.3	2.9	18.2	2.2	41	0.7	<1.4	105
67 A	<0.005	56.5	28.00	3.4	0.3	4.0	32.5	22.6	32	<0.7	<1.1	430*
68 A	0.427*	800.0*	18.60	6.0*	0.5	8.6	27.5	34.4	317*	0.5	<1.5	206
97 A	0.380*	1370.0*	43.00*	<0.4	<0.3	2.4	15.3	5.2	<25	1.3	<1.9	80
99 A	0.002	60.0	7.15	0.7	<0.2	2.9	19.8	<3.6	<25	<0.4	<1.5	420*
102 A	0.010	41.0	0.84	9.9*	0.6	6.4	31.0	18.2	222*	7.5*	<1.6	4100*
54 A	0.023	69.5	4.25	0.7	<0.1	3.4	16.1	2.4	43	1.4	<1.1	37
61 A	<0.005	0.4	41.00*	<0.2	<0.3	3.2	20.1	8.4	<26	<0.7	<1.5	604*
164 A	<0.009	59.0	15.50	0.5	0.4	6.0	24.3	2.0	116	8.2*	1.7	162
166 A	<0.008	14.1	13.00	0.4	<0.3	6.3	57.0	2.0	32	<0.7	2.6	297
167 A	1.450*	5750.0*	41.50*	4.2	0.3	3.1	20.4	2.0	97	3.6	1.8	47
168 A	0.010	8.6	2.45	<0.5	0.2	4.3	64.0	6.4	29	1.2	2.7	500*
170 A	<0.010	124.0	49.50*	2.3	0.4	2.5	33.5	2.0	32	<0.8	<2.2	171
171 A	<0.011	190.0*	13.30	<0.6	1.1	7.0	25.1	13.8	65	<0.5	<1.7	181
173 A	0.410*	1580.0*	33.00	4.8*	<0.3	2.8	14.2	2.0	115	<0.5	<1.5	39
174 A	<0.009	22.1	88.50*	2.5	0.3	4.4	20.4	2.0	88	13.0*	<1.6	820*
$\bar{x}$ (22 sampl.)	0.140	512.1	26.9	3.3	0.6	4.2	25.4	12.4	88	2.2	1.6	398
X*	0.013	56.1	15.20	1.3	—	—	—	—	69	1.1	—	121
45 A	<0.005	19.7	0.50	<0.3	<0.1	1.8	46.5	<3.4	<25	<0.4	<1.9	173
49 A	<0.004	385.0*	0.82	1.7	<0.1	10.3*	27.0	<2.4	<22	<0.3	<1.4	280*
50 A	0.145*	450.0*	125.00*	<0.4	<0.4	1.32	35.0	2.0	<36	<0.7	<1.9	130
57 A	<0.004	44.5	6.15	1.9	0.5	5.2	17.0	12.2	57	1.0	<1.1	53
94 A	0.014	11.5	0.34	0.7	0.3	2.3	11.8	18.8	108	3.9	<0.9	72
98 A	0.040	49.5	1.55	2.2	0.4	3.5	26.2	12.8	56	3.4	<1.4	41
100 A	<0.005	21.0	0.69	<0.4	<0.2	2.5	77.0	<5.2	<29	<0.5	<2.4	214
104 A	<0.005	6.0	0.40	<0.4	<0.2	2.3	56.5	22.6	<29	<0.5	<2.0	2100*
172 A	1.050*	6300.0*	139.00*	2.8	0.6	1.6	13.6	13.4	37	0.4	<2.0	48
$\bar{x}$ (9 sampl.)	0.140	809.7	30.49	1.3	0.4	3.6	34.5	10.2	44	1.3	1.6	345
X*	0.011	152.2	1.49	—	—	2.5	—	—	—	—	—	104
$\bar{x}$ (31 sampl.)	0.140	598.5	27.94	2.7	0.5	4.0	28.0	11.8	75	1.6	1.6	382
X*	0.012	83.5	11.35	1.1	—	3.7	—	—	61	1.2	—	116

Table 38 a

Contents of trace elements in the black shales of B, C type from the productive zones

Sample number	La	Ce	Sm	Eu	Tb	Yb	Lu	ΣREE	Th	U
40 B	20.2	20.0	5.0	0.9	0.7	2.6	0.6	47.5	1.3	5.5
42 B	6.4	8.6	1.6	0.9	0.1	1.4	0.2	18.4	0.7	3.5
48 B	50.8	11.6	16.2	2.7	1.8	8.1	1.2	84.3	3.7	33.5
52 B	1.2	1.5	1.0	0.7	0.2	1.3	0.2	5.6	<0.3	2.5
53 B	17.0	17.1	4.4	0.7	0.4	2.7	0.4	40.5	0.8	4.3
70 B	24.2	34.0	7.0	1.3	0.8	3.8	0.6	68.2	3.2	8.3
82 B	15.7	65.7	3.4	1.7	0.6	1.5	0.2	87.1	10.5	<0.3
84 B	12.8	45.4	1.2	1.0	0.7	1.4	0.2	62.1	5.3	0.9
146 B	1.4	3.4	0.6	0.7	0.3	0.9	0.1	7.1	<0.3	2.8
43 C	15.5	36.0	3.2	1.3	0.8	1.9	0.4	57.5	4.4	2.4
47 C	23.8	19.6	5.6	1.3	0.8	2.9	0.4	51.6	<0.3	2.5
55 C	38.8	28.6	11.8	2.4	1.1	6.0	0.9	83.7	1.7	20.7
71 C	25.6	55.3	5.6	1.0	0.6	1.5	0.3	87.1	8.3	2.4
165 B	22.6	25.4	8.0	1.6	1.0	4.0	0.8	59.4	4.9	9.5
169 B	25.6	28.6	5.0	0.8	1.0	1.7	0.4	60.6	7.7	3.3
$\bar{x}$ (15 sampl)	20.1	26.7	5.4	1.3	0.7	2.8	0.4	54.8	3.5	6.8
Prod. zones in all 46 sampl.	16.8	28.0	4.6	1.3	0.6	3.0	0.5	52.6	3.7	7.3

Further explanations in Table 37 a.

the neutron-flow density put into irradiation container.

Irradiation was performed in the active zone of a VVR — S reactor in Řež for three hours, with the density of neutron flow of $3—5 . 10^{17}$ $m^{-2}s^{-1}$. After two-days' cooling the samples were transferred into the Radiometry Department in Stráž pod Ralskem, where the polyethylene cases were taken out from Al wrapping and sealed in clean polyethylene bags.

The radiation spectra of gamma-activated samples were measured twice, after 3 and 26 days, respectively with a computer gamma-spectrometer CANBERRA — JUPITER 80 (USA).

The measuring apparatus consisted of a coaxial Ge(Li) detector (efficiency 10 %, resolution FWHM 1.8 keV for energy 1332.4 keV ^{60}Co, the peak/Compton ratio 37:1), a preamplifier 2001, an amplifier 2020, convertor ADV 8080 and analyser S 80.

The measured spectra were processed on a computer PDP 11/344 (128 kB, operation system RSX-11M), using a modified Spectran F programme (Canberra — Technical Reference Manual for Spectran F Version 2, Canberra Ind., Meriden, 1981).

Detection limits were computed for every sample separately, according to criteria proposed by Currie (1968) and developed further by other workers (Obrusnik et al., 1978; Kotas et al., 1979). This procedure is more appropriate than the currently used procedures, because it involves interferences cau-

Table 38 b

Contens of trace in the black shales of B, C type from the productive zones

Sample number	Au	As	Sb	W	Ta	Hf	Sc	Ga	Rb	Cs	Ag	Zn
40 B	<0.004	252.0*	26.60	2.9	<0.2	0.4	5.9	21.2	<30	1.3	<2.8	81
42 B	<0.004	161.0*	22.00	2.0	<0.2	1.6	8.6	<1.8	<26	0.4	<1.2	36
48 B	0.031	355.0*	3.30	1.5	0.7	1.1	11.7	<2.4	<37	<0.4	<1.6	1020*
52 B	<0.006	480.0*	10.70	<0.3	<0.2	2.3	33.5	17.6	93	3.3	<1.8	210
53 B	0.025	85.5	4.50	1.5	<0.1	2.5	12.4	17.8	<21	1.4	<1.1	32
70 B	0.029	100.0	15.40	3.0	0.3	3.4	12.3	18.0	87	<0.5	<1.1	110
82 B	<0.004	23.0	0.53	2.4	0.7	7.8	26.6	5.6	304*	6.0	<1.4	131
84 B	<0.008	279.0*	156.00*	0.9	<0.5	6.4	21.2	<5.2	38	<1.3	<1.8	147
146 B	0.018	86.0	6.65	0.3	<0.2	1.5	36.0	47.0	<27	4.7	<1.8	182
43 C	<0.005	150.0*	35.50	1.8	<0.3	3.3	25.5	<2.2	82	2.7	<1.6	147
47 C	0.036	400.0*	5.40	1.2	<0.2	1.4	5.8	<5.6	<36	<0.4	<1.4	132
55 C	0.023	305.0*	3.70	1.1	<0.2	1.4	6.3	<1.6	<32	<0.4	<1.3	655*
71 C	0.023	128.0*	25.50	8.3	0.5	4.6	23.8	30.6	230*	<0.6	<1.5	90
165 B	0.011	101.0	18.30	0.7	0.7	8.5	38.0	2.0	93	<0.6	2.1	350
169 B	0.010	20.6	26.0	3.5	0.5	7.3	26.8	2.0	188	4.5	1.9	53
x̄ (15 sampl.)	0.017	215.7	34.95	2.1	0.3	2.9	17.7	13.6	80	1.8	1.6	229
X*	—	69.3	14.58	—	—	—	—	—	61	—	—	131
Prod. zones in all 46 samples	0.044	208.8	23.05	2.2	0.3	3.5	23.6	12.4	79	1.5	1.5	360

Further explanations in Table 37 a.

Table 39 a

Contents of trace elements in heavy fractions from the mineralized slates and ores of productive zones

Sample number	La	Ce	Sm	Eu	Tb	Yb	Lu	ΣREE	Th	U
40 B/TP	8.2	1.9	1.6	0.7	0.3	2.1	0.2	14.2	0.6	2.8
42 B/TP	4.3	1.5	0.2	0.4	<0.2	0.7	0.3	7.5	0.3	3.4
43 C/TP	5.8	1.5	1.0	0.5	0.4	1.5	0.3	10.5	0.5	6.3
47 C/TP	16.0	2.1	2.2	0.8	0.3	1.4	0.2	21.9	<0.3	2.6
48 B/TP	43.4	37.8	7.0	2.0	1.4	6.4	0.9	95.4	3.3	27.0
52 B/TP	1.2	1.9	0.4	0.2	<0.5	0.7	<0.1	4.8	<0.3	3.6
53 B/TP	18.4	1.2	2.4	0.6	0.5	2.1	0.3	24.3	0.5	3.5
55 C/TP	33.2	22.7	6.0	2.1	1.3	5.2	0.7	68.2	0.9	19.1
70 B/TP	1.6	36.9	0.4	0.7	0.2	<0.6	<0.3	40.5	4.9	<0.8
71 C/TP	7.4	12.1	0.2	0.5	0.4	1.5	0.3	22.3	1.2	12.7
$\bar{x}$ (10 sampl.)	13.9	11.9	2.2	0.8	0.5	2.2	0.4	30.8	1.3	11.2

Further explanations in Table 37 a.

Table 39 b

Contents of trace elements in heavy fractions from the mineralized slates and ores of productive zones

Sample number	Au	As	Sb	W	Ta	Hf	Sc	Ga	Rb	Cs	Ag	Zn
40 B/TP	0.008	700.0	11.00	1.2	<0.2	<0.4	1.9	<3.4	<43	<0.5	1.5	236
42 B/TP	0.015	365.0	11.70	1.8	<0.2	0.7	4.9	<3.4	<34	<0.4	1.3	66
43 C/TP	0.010	545.0	5.80	1.4	<0.2	<0.4	2.6	<3.4	<43	<0.4	1.5	162
47 C/TP	0.037	655.0	4.15	0.7	<0.2	<0.4	2.9	<3.6	<45	<0.4	2.3	143
48 B/TP	0.027	480.0	2.57	0.9	<0.2	1.5	7.4	<4.4	<43	<0.4	1.6	820*
52 B/TP	0.026	985.0	12.90	0.4	<0.6	<0.4	10.6	<4.8	<45	<0.4	1.7	147
53 B/TP	0.034	208.0	4.15	0.7	<0.1	1.3	7.8	<12.4	<30	<0.4	1.3	58
55 C/TP	0.026	405.0	3.15	1.6	<0.2	1.1	5.3	<15.6	<42	<0.4	2.5	555
70 B/TP	0.350	890.0	515.00*	<1.2	<0.9	1.8	15.7	<21.0	115	<1.2	2.9	144
71 C/TP	0.029	28.1*	2.82	2.7	<0.6	1.0	8.0	<13.0	<40	0.6	1.6	495
$\bar{x}$ (10 sampl.)	0.056	526.1	57.3	1.3	1.2	0.9	6.7	8.4	48	0.5	1.8	283
X*	—	28.1	6.47	—	—	—	—	—	—	—	—	223

Further explanations in Table 37 a.

sed by the presence of even minute amounts of disturbing admixture, and those caused by changes in background values as well. The change may be provoked by increase in concentration of a macrocomponent in the sample.

In using this procedure a question arises which numerical value should be applied in correlation and statistical calculations for values $< x$. Geochemical workplace in ÚL ČSUP uses the following procedure: To compute the value according to relation $y = 0.5\ x$, when the number of samples with values $< x$

Table 40 a
Contents of trace elements in the slates outside the productive zones

Sample number	La	Ce	Sm	Eu	Tb	Yb	Lu	ΣREE	Th	U
108 A	23.6	53.5	5.2	1.2	0.6	3.2	0.5	85.2	6.8	3.0
111 A	24.0	64.3	2.8	1.1	0.8	2.0	0.5	94.1	8.4	1.4
112 A	29.2	64.8	4.4	1.1	0.5	2.0	0.4	100.2	7.0	1.7
125 A	36.4	86.4	4.0	1.5	0.7	2.5	0.5	130.0	11.2	2.7
130 A	21.8	46.8	3.4	0.9	0.4	1.4	0.2	73.2	6.5	0.8
131 A	24.8	54.9	2.6	1.1	0.4	1.3	0.3	84.1	5.1	<0.4
132 A	27.2	58.9	3.4	1.3	0.5	1.3	0.2	91.1	7.5	<1.4
133 A	22.4	60.7	2.8	1.4	1.0	1.9	0.3	89.1	8.0	<0.4
141 A	17.6	56.7	4.0	0.8	0.4	2.0	0.4	79.9	8.1	1.3
144 A	23.6	50.4	3.0	1.1	0.5	2.3	0.3	79.7	8.2	1.9
149 A	24.0	57.6	3.2	1.2	0.7	1.8	0.3	87.2	6.4	0.9
151 A	35.8	77.4	5.6	1.3	0.5	1.3	0.3	119.4	12.3	0.5
152 A	20.6	47.7	4.8	1.1	0.5	2.0	0.4	74.7	7.1	<0.4
155 A	19.0	42.3	3.6	0.9	0.4	2.7	0.3	67.4	8.3	1.5
158 A	26.8	63.4	5.6	1.5	0.5	1.7	0.3	97.0	7.2	<0.4
147 B	29.0	59.4	3.8	1.0	0.5	1.7	0.3	93.8	7.1	1.6
157 B	24.0	51.7	2.8	0.8	0.3	0.8	0.2	79.2	4.5	0.3
162 B	15.2	17.3	4.0	0.7	0.7	2.4	0.6	38.9	4.2	5.0
$\bar{x}$ (18 sampl.)	24.7	56.3	3.8	1.1	0.5	1.9	0.3	86.8	7.4	3.1

Further explanations in Table 37 a.

Table 40 b
Contents of trace elements in the slates outside the productive zones

Sample number	Au	As	Sb	W	Ta	Hf	Sc	Ga	Rb	Cs	Ag	Zn
108 A	0.010	18.5*	0.97	0.8	0.5	9.2*	22.4	28.2	298*	3.0	<1.3	88
111 A	<0.005	2.9	0.59	<0.4	0.7	6.6	29.7	40.6	136	10.5*	<1.7	153
112 A	<0.004	4.7	1.10	<0.3	0.4	6.4	23.8	<5.4	243*	5.7	<1.5	165
125 A	<0.005	8.0	0.90	<0.5	<0.4	10.3*	22.0	32.6	208	3.0	<1.4	192
130 A	<0.004	2.3	0.18	<0.3	0.3	7.2	16.6	<6.0	73	2.4	<1.2	186
131 A	<0.005	8.3	0.34	<0.5	0.5	5.4	21.6	<8.8	70	3.7	<1.4	146
132 A	<0.010	2.6	0.26	<0.4	0.4	8.3*	21.9	14.0	101	2.3	<1.4	305*
133 A	<0.005	15.4*	3.85*	<0.5	0.4	6.8	31.5	26.4	59	5.0	<1.6	405*
141 A	<0.004	3.4	1.16	3.1	0.5	6.7	32.0	19.2	223*	11.5*	<1.7	203
144 A	<0.005	2.6	0.64	<0.5	<0.1	7.4	28.2	9.4	94	5.2	<1.5	181
149 A	<0.005	4.2	0.10	<0.5	0.4	7.5	22.1	38.8	134	3.3	<1.4	126
151 A	<0.005	4.2	0.64	<0.5	0.6	6.8	23.1	36.8	106	7.5	<1.5	122
152 A	<0.005	5.2	0.15	<0.5	0.5	8.6*	20.5	54.0	66	1.0	<1.4	176
155 A	<0.005	1.1	0.84	<0.5	0.5	6.8	30.0	44.0	72	4.7	<1.6	187
158 A	<0.005	7.3	0.17	<0.6	1.3	7.6	26.8	26.2	106	3.7	<1.6	196
147 B	<0.005	11.5*	0.28	<0.4	0.5	7.4	20.3	<8.4	104	1.8	<1.4	300*
157 B	<0.004	7.4	0.44	<0.4	0.3	5.1	14.1	42.4	<17	2.4	<1.1	141
162 B	0.009	1.4	0.07	0.5	1.2	10.5*	21.0	2.0	119	2.4	1.4	79
$\bar{x}$ (18 sampl.)	0.005	6.1	0.70	0.7	0.5	7.5	23.7	24.6	123	4.4	1.4	186
x*	—	4.4	0.52	—	—	6.7	—	—	97	3.6	—	150

Further explanations in Table 37 a.

Table 41 a

Contents of trace elements in the slates from the Harmónia Group

Sample number	La	Ce	Sm	Eu	Tb	Yb	Lu	ΣREE	Th	U
17 A	26.2	102.6	2.6	1.5	1.2	3.0	0.4	136.2	17.2	0.7
19 A	27.4	58.0	5.2	1.2	1.2	2.3	0.3	93.0	16.8	17.5
92 A	21.0	52.6	4.0	1.0	0.4	1.5	0.3	78.8	8.5	2.6
107 A	34.8	74.7	4.8	1.3	0.8	1.7	0.3	116.0	13.0	2.0
110 A	34.8	78.3	2.6	1.2	0.5	2.3	0.3	118.7	14.0	1.0
113 A	16.6	35.1	2.4	0.8	0.5	0.9	1.2	56.3	6.5	0.7
121 A	20.8	48.6	4.4	1.1	0.4	2.5	0.5	76.1	76.1	2.4
122 A	41.4	86.8	5.8	1.1	0.5	1.9	0.2	134.8	16.9	3.2
128 A	27.6	61.6	6.4	1.2	0.7	2.6	0.5	97.4	7.8	2.8
129 A	24.8	61.2	4.8	1.2	0.7	1.2	0.2	91.7	7.3	<0.3
134 A	39.0	85.5	6.6	1.8	0.8	2.2	0.4	133.0	9.9	2.6
136 A	40.2	90.0	0.2	1.4	0.6	2.2	0.4	134.9	10.8	3.4
145 A	26.6	41.8	4.8	1.2	0.6	3.4	0.5	76.5	4.1	10.5
156 A	31.0	48.6	3.8	0.6	0.2	1.3	0.7	84.3	4.5	5.5
160 A	29.0	68.8	4.8	1.3	0.6	1.9	0.3	104.3	8.4	1.7
114 B	10.6	27.4	1.2	0.5	0.2	1.3	0.4	41.0	4.0	2.4
$\bar{x}$ (16 sampl.)	28.2	63.8	4.0	1.1	0.6	2.0	0.4	98.1	9.8	3.7

Further explanations in Table 37 a.

Table 41 b

Contents of trace elements in the slates from the Harmónia Group

Sample number	Au	As	Sb	W	Ta	Hf	Sc	Ga	Rb	Cs	Ag	Zn
17 A	<0.004	0.6	0.11	0.6	<1.0	4.8	31.5	17.8	324*	7.6*	<1.4	233*
19 A	0.022	3.2	0.49	0.9	1.1	5.6	21.7	27.6	234*	5.5	<1.3	103
92 A	0.013	420.0*	0.68	1.4	1.1	5.5	37.0	33.2	214	<0.4	<1.7	192
107 A	<0.004	17.8	0.21	0.8	0.5	6.7	28.4	39.0	200	5.0	<1.5	191
110 A	<0.005	2.7	0.15	<0.4	0.9	6.2	34.0	24.6	231*	6.2	<1.2	157
113 A	<0.006	8.6	0.22	<0.4	0.4	4.0	13.2	12.6	88	4.0	<1.1	121
121 A	0.020	85.0*	3.65*	<0.4	0.5	7.9	20.8	<7.0	103	1.8	<1.4	161
122 A	0.011	79.5*	0.61	1.2	1.1	5.9	27.7	62.0	296*	8.1*	<1.6	184
128 A	0.019	24.6	0.92	<0.3	0.6	7.6	28.2	<5.8	174	6.3	<1.5	165
129 A	<0.004	29.1	0.10	<0.4	0.6	7.6	24.1	43.8	96	1.8	<1.4	127
134 A	<0.004	10.2	1.05	1.4	0.6	7.8	31.5	<6.6	185	3.6	<1.7	141
136 A	0.010	8.3	0.35	<0.4	1.0	6.6	29.8	45.6	206	9.5*	<1.6	212
145 A	0.009	10.0	1.50	3.1	0.4	5.1	22.0	37.2	98	1.8	<1.4	420*
156 A	0.009	1.8	0.37	0.3	0.3	2.0	9.6	17.4	93	3.5	<0.9	86
160 A	<0.004	9.3	0.08	<0.5	0.4	9.6	21.2	27.4	82	1.6	<1.4	134
114 B	<0.005	1.6	0.17	<0.5	0.4	8.8	22.9	5.2	74	1.4	<1.3	45
$\bar{x}$ (16 sampl.)	0.009	44.5	0.66	0.8	0.7	6.3	25.2	25.8	168	4.2	1.4	167
X*	—	9.8	0.47	—	—	—	—	—	134	3.3	—	144

Further explanations in Table 37 a.

for a given element is lower than 30 %. Some authors (e.g. Dr. J a k e š, Geological Survey, Prague) employs the relation $y = 0.4\ x$. If the number of samples with the values of detection limits $< x$ is higher than ca. 30 %, the average value of detection limit is computed for the whole set, and the values of the respective element should not be used for correlation purposes.

The present authors did not employ these relations in computing the arithmetic means, but the relation $y = x$, because the difference between the half and whole value for $< x$ is so small that it is within the limits of admissible error of the method.

Elements of rare earths

Data on the contents of rare earths elements (TR or REE in the further text) in black shales are rather sporadic. In the literature the REE contents are often given for sediments without a more detailed description (the rock is, e. g., termed shale only). In the last twenty years the analytical methods have been greatly improved and refined and neutron activation has been used successfully for the analysis of REE. At the present time much attention is focussed on the REE, because their contents can be employed in solving petrogenetic problems of igneous and metamorphic rocks, in particular; the sediments have been rather neglected.

The REE occur chiefly as trivalent cations; Eu is also known in the form of Eu^{2+} and cerium as Ce^{4+}. They are divided into two subgroups: the lighter cerium subgroup (from La to Gd) showing properties of higher basicity, and the heavier yttrium subgroup (from Tb to Lu) of a lower basicity. Yttrium is often classed to this group in computations. The essential factor controlling the distribution and redistribution of REE in geological processes are the volume ratios of ions. The REE contents are generally given in values normalized to their contents in chondrites, assuming that the composition of chondrites corresponds to the primary composition of the Earth, i. e. to the composition before differentiation and genesis of geospheres.

The study of the REE contents in sediments is based on correlation of the analytical data with the data published by H a s k i n et al. (1968) for the shales of North America, not described to any detail. This correlation, however, must be made with care, because the N. American slates are very likely mature and homogenized mineralogicaly by metamorphism, whereas most of the Malé Karpaty black slates contain relics of mineral, mainly feldspar clasts in the homogenized matrix (especially in the Harmónia Group). Table 42 compiles data on the contents of and REE in slaty sediments; the data in columns 4 and 5 relate to rocks similar to the rocks under study. The rocks from the productive zones with anomalous mineral paragenesis, in which the contents of some components increase (C_{org}, sulphides, quartz, carbonates, amphiboles) have therefore varying contents of REE (mainly those with a great ionic radius) and anomalous ratios of elements. For this reason we have ranged these slates (type A) from productive zones, chiefly with anomalous La/Ce ratio to a separate subgroup (Table 37). A similar situation occurs in slates rich in pyrite or in pyrite-pyrrhotite ores.

The REE contents of black slates of the Malé Karpaty crytalline complex were determined from 90 analyses made by INAA method in the Central La-

Table 42

Compiled data of REE contents in the various slates (g . t^{-1})

	1	2	3	4	5
La	41.1	32.0	28.0	20.0	19.5
Ce	85.9	73.0	49.0	42.0	36.0
Sm	7.3	5.7	3.9	5.6	3.9
Eu	1.5	1.2	0.8	1.1	0.5
Tb	1.0	0.8	0.4	0.6	0.5
Yb	3.3	3.1	1.8	1.8	1.4
Lu	0.6	0.5	0.4	0.3	0.2

Explanations: 1 — mean from 36 European Palaeozoic slates (Haskin et al., 1968); 2 — mean from 40 North American slates (Haskin et al., 1968); 3 — mean from 4 analyses of American samples, pre-Cambrian to Carboniferous (Haskin — Gehl, 1962); 4 — black shale, Cansas, USA (Haskin — Gehl, 1962); 5 — black graphitic shale, Krivoj Rog, U.S.S.R. (Tugarinov et al., 1973).

boratory of the Czechoslovak Uranium Industry at Stráž pod Ralskem. Because of analytical difficulties the analyses were twice repeated, and the results of REE and other trace elements here evaluated are corrected values. The set of samples was divided into partial sets according to criteria given in the foregoing chapters.

The table summarizing the average REE contents in the rocks studied (Table 43) shows clearly that the analyses of heavy fractions separated from the original samples cannot be involved in the total set and computations of arithmetic means, because of very low contents of light REE (La and Ce). This anomaly is obviously caused by a large amount of sulphidic minerals present in the heavy fractions. Nine samples with extremely low contents of La, Ce and Sm were also excluded from the samples coming from the productive zones (type A).

Generally, the REE contents in the slates of productive zones are relatively low, compared with the data in the literature concerning common metapelites and black shales. According to our investigations, the organic matter in rocks combined with more or less sulphides or carbonates, or increased contents of quartz and/or mafic minerals from amphibole group strongly disturbs the contents and ratio of La and Ce which, in contrast, is relatively stable in clayey-siliceous sediments and their metamorphites. Table 42 and Table 8 in Chapter II list the contents of REE relatively close to those in the rocks of productive zones in the Malé Karpaty. The set of samples from the productive zones was divided into two parts; one corresponds to clayey siliceous metamorphites according to the REE contents, whereas the other displays unusual contents of La and Ce other elements, and thus also their ratios. The slates with anomalous contents of REE probably developed under particular sedimentary conditions, in the period of submarine volcanic-metallogenic activity, or they were additionally influenced by hydrothermal processes and other metamorphic events.

Table 43

REE contents in black shales from the Malé Karpaty crystalline complex.
(Summary table, contents in g . t^{-1})

	All set of samples 80 sampl.	Productive zones					Outside productive zones 18 sampl.	Harmónia Group 16 sampl.	Heavy fractions 10 sampl.
		Type A			Type B,C 15 sampl.	In all 46 sampl.			
		22 sampl.	9 sampl.	Together 31 sampl.					
La	20.8	19.8	4.1	15.2	20.1	16.8	24.7	28.2	13.9
Ce	41.5	32.1	20.4	28.7	26.7	28.0	56.3	63.8	11.9
Sm	2.1	2.8	0.9	2.2	2.7	2.3	1.9	2.0	1.1
Eu	1.3	1.6	0.8	1.4	1.3	1.4	1.1	1.1	0.8
Tb	0.6	0.8	0.3	0.6	0.7	0.6	0.5	0.6	0.5
Yb	2.5	3.8	1.4	3.1	2.8	3.0	1.9	2.0	2.2
Lu	0.4	0.7	0.2	0.5	0.4	0.5	0.3	0.4	0.4
REE	69.2	61.6	28.1	51.7	54.8	52.6	86.8	98.1	30.8

The content of organic matter also causes a special distribution of REE with a predominance of intermediate members (B a l a š o v, 1976), (Fig. 31).

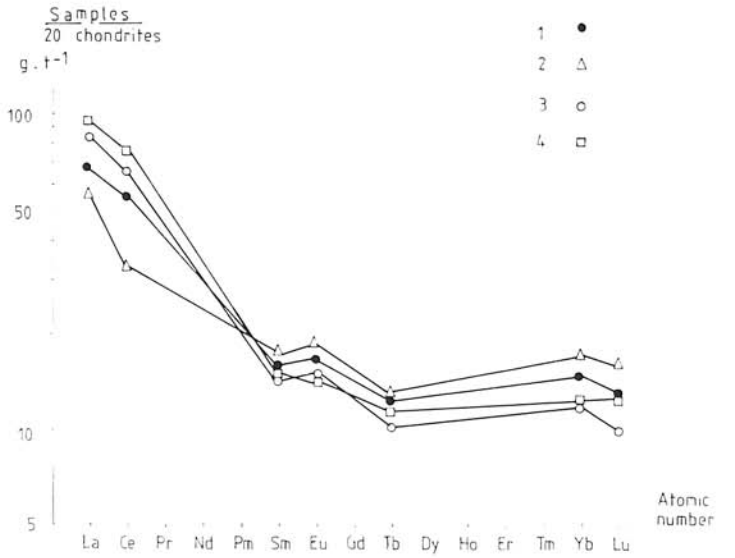


Fig. 31. Graph of normalized REE contents to 20 chondrites in the black shales of the Malé Karpaty crystalline complex.
Explanations: 1 — whole set of 80 samples; 2 — productive zones of 46 samples altogether; 3 — out of zones 18 samples; 4 — Harmónia Group 16 samples.

As concerns the La and Ce contents, the samples from areas outside the productive zones and from the Harmónia Group provide a different geochemical pattern. These samples contain less organic matter and belong to rocks that were enriched in lighter members of REE either primarily or due to metamorphic redistribution. As a result, the contents of intermediate and heavier components of TR, such as Sm, Eu, Tb, Yb and Lu decrease (see Fig. 31). From the constant La/Ce ratio in these samples it can be inferred that sedimentation of the shale material in these areas occurred under quieter conditions, without basic volcanic activity, which exerted influence on sedimentation of rocks of the pyrite-bearing zones.

It is remarkable that the rock samples from the Harmónia Group have the highest REE average contents of all the Malé Karpaty samples. This may provide evidence for its being younger than the underlying schists. The enrichment of younger sediments in REE relative to the older ones is reported by Wildeman — Haskin (1973). The younger age of the Harmónia Group was determined both stratigraphically and radiometrically (see Chapter I). The opinion of these authors is supported by the data on REE contents in the sediments of the Bohemian Massif recorded by Čadková — Mrázek (1980). They obtained the following sums of REE contents in $g \cdot t^{-1}$ (the rocks in the Table are arranged chronologically):

Age	Rocks	REE
Upper Proterozoic	metapelites	71.5
Central Bohemian Cambrian	pelites	78.7
Devonian	shales	93.0
Lower Carboniferous	pelites — shales	123.3
Upper Carboniferous	aleuropelites	164.3

We note that our summary REE values given in the Tables are lower also because that several elements, including Y, are lacking; they would increase the sum Σ REE considerably, but the rising values with age are distinct even when the representation of elements is incomplete.

The authors hope that further still more detailed study of REE contents in black slates of the Malé Karpaty crystalline complex will permit them to advance their knowledge of the derivation of organic matter, and of metamorphic and sedimentary history of these rocks and their age as well. For the time being there are no data available on the contents of other important elements such as Pr, Nd, Gd, Dy, Ho, Er, Tm and Y. The great absence of Gd is responsible for inexact determination of the positive or negative Eu anomaly. Therefore it is planned to subject several selected samples to combined neutron activation and X-ray fluorescence analyses. Of many data recorded we selected for comparison the values published for sediments by Kay (1972 in Fairbridge, 1972). The author does not mention which rocks and in which ratio are included in the average values. The values are given in $g \cdot t^{-1}$ (ppm).

La ~ 39;	Ce ~ 75;	Pr ~ 10;	Nd ~ 37;	Pm	not given
Sm ~ 7	Eu ~ 2	Gd ~ 6.1	Tb ~ 1.3	Dy ~ 6	
Ho ~ 1.4	Er ~ 4	Tm ~ 0.58	Yb ~ 3.4	Lu ~ 0.6	Y ~ 35

The behaviour of REE and other elements in metamorphism poces a specific problem. The slates of the Malé Karpaty area are metamorphosed to different grades, depending on the distance from granitoid apophyses. The influence of metamorphism on the variation of elements is very significant and some conclusions have already been reported on in Chapter III, as e.g. the decrease in As, Sb, U and Hg with metamorphism. Relevant papers on this question were published by the workers of the Mining Academy in Freiberg under the guidance of prof. Rösler (Beuge — Rösler et al., 1978; Beuge, 1976; Rösler, 1980; Rősler — Beuge et al., 1977). They arrived at the conclusion that many elements that were regarded as almost immobile, may be mobilized under the influence of metamorphism. The elements Hg, As and F appear to be the least isochemical.

The conclusions on the migration of elements were based on the analyses of pelitic and clayey-siliceous rocks metamorphosed at different grades (see Table 44). The finding that the average contents of As and Hg are somewhat higher and the Sc and Sr values a little lower, the author considers to be a geochemical characteristic of the region and not an analytical error. The elements F, Cl, Br and I escape with water, but fluorine remains in the rock up to higher temperatures. The elements Au and Ag are reduced in amount with increasing metamorphic grade, Sr increases in amount, and Sc behaves as rare earths. Despite the negative Eu anomaly, the rare earths (TR, REE) decrease with increasing metamorphism.

The authors of this paper also studied the contents of several microelements in relation to the metamorphic grade; the results of their investigations are plotted in graph 7.

Tungsten

The highest average contents of tungsten have been determined in samples from the productive zones (rocks of A type — 2.7 g . t^{-1}, and up to 3.3 g . t^{-1} after eliminating the anomalous samples). The value of the bulk W content for the productive zone (i.e types, A, B, C) is 2.5 g . t^{-1}, which is consistent with the value given for carbonaceous shales of India by Dekate (1967) in Krauskopf, 1970. Samples from the areas outside the productive zones and from the Harmónia Group have very low values of tungsten (0.7 and 0.8 g . t^{-1}), i.e. samples containing less organic matter and showing lower metamorphism of granite. Such a correlation of W with organic matter was described by several authors (e.g. Jeffery, 1959; Pargeter, 1956 in Krauskopf, 1970); all of them point out that they are few reliable data to substantiate this relationship. Taylor (1965) presented a value of 2 g . t^{-1} W for arkoses and shales. It is to be noted that the average W value of 7.52 g . t^{-1} obtained by INAA method for metabasites of the Malé Karpaty is to be regarded as exaggerated (Cambel — Kamenický, 1982).

Tantalum

There are few data available on the Ta contents in sediments. Pachadžanov (1963), in Wedepohl, 1978, Handbook of Geochemistry II/5, gives an

Table 44

Contents of elements in 8-grade metamorphic profile according to Rösler et al., 1980. Contents in g . t^{-1}, Au, Ag and I contents in ppb

	Clay mud	Clay	Clay-stone	Clay shale	Phyllite	Mica schist	Gneiss	Granulite
Br	29.2	6.8	1.2	1.2	1.3	1.2	1.7	1.3
I	2380	1800	410	90	86	42	35	97
Cl	7890	3200	105	46	35	58	89	97
As	7.8	16.7	17.1	(41.1)	14.6	6.8	0.9	1.1
Sb	0.73	1.94	2.53	0.66	0.80	2.05	0.23	0.27
Ba	675	235	420	432	460	690	640	295
Sr	171	171	161	166	201	242	223	243
Rb	181	122	128	93	198	186	142	69
Cs	7.7	8.6	15.5	8.5	9.3	9.0	5.9	2.6
Au	2.4	1.8	1.5	1.0	1.0	0.7	0.9	1.2
Ag	300	140	290	200	80	180	90	100
Co	22.8	23.7	36.0	28.5	28.8	34.3	31.1	21.2
Ni	47	81	92	57	78	85	68	90
Th	21.0	10.7	11.3	19.5	14.2	13.6	13.4	9.2
U	4.1	2.3	3.2	4.0	2.5	4.3	2.4	0.9
Ta	1.55	1.05	1.02	1.56	1.28	1.43	1.37	1.22
Hf	5.9	6.1	5.1	10.2	4.9	5.7	6.4	3.2
Sc	20.2	13.7	16.2	18.8	21.8	21.9	20.4	19.7
La	87	52	54	75	70	68	61	58
Ce	138	77	75	102	95	94	92	89
Nd	64	34	29	60	52	39	39	50
Sm	9.7	5.8	6.0	8.2	7.9	8.2	6.9	5.0
Eu	1.95	1.32	1.25	1.55	1.81	1.93	1.55	1.16
Tb	1.41	0.88	0.87	1.25	1.22	1.31	1.14	0.63
Yb	4.3	3.0	3.3	4.3	4.2	5.0	4.5	1.7
Lu	0.51	0.33	0.35	0.45	0.44	0.66	0.38	0.20

average value of 2 g . t^{-1} for the shales of the Russian Platform. Pelitic material from a humid environment is evidently richer in Ta (2.4 g . t^{-1}) than from an acid environment (0.9 g . t^{-1}). The Ta contents in black slates of the Malé Karpaty crystalline complex are lower than whatever value presented in the literature. The reduction may be accounted for by the use of the INAA method, as Flörke et al. (1978) described a similar decrease in Ta contents on marine clays analysed by this method. Cambel et Kamenický (1982) share this opinion, because the values obtained in the laboratory at Stráž pod Ralskem for

Table 45

Contents of trace elements in graphitic phyllites of Keno Hill — Galena Hill area, Yukon. Adapted according to Gleeson — Boyle (1980).
Contents in g . t^{-1}

	Graphitic phyllites								$\bar{x}$
Cu	24	72	40	72	20	52	20	12	39
Pb	2.5	5	20	2.5	2.5	2.5	65	5	13
Zn	120	60	40	120	10	30	110	60	69
Ni	80	15	2.5	2.5	10	40	55	2.5	26
Co	2.5	2.5	2.5	2.5	2.5	5	2.5	2.5	2.5
As	8	6	1	1	1	1	1	1	2.5
Sb	3	0.5	1	1	2	0.5	0.5	1	1.2
Mo	17	0.5	0.5	4	20	5	1.0	2	6.2
W	2	2	2	2	2	2	2	2	2
U	13.5	1.1	1.9	3.9	2.3	4.7	2.7	1.9	4
Sn	3	7	3	4	5	10	9	9	4
Ag	1	0.2	0.3	0.8	0.6	0.6	ND	ND	0.5
Ba	6757	1152	4146	1960	537	1508	1615	2592	2533

tungsten in West Carpathian metabasites are almost ten times lower than the data reported in the literature. It is not possible to establish a dependence or change of content values for the black slates of the productive zones or other Malé Karpaty areas, because the differences in Ta contents from various shale complexes are small. In other aspects the geochemistry of Ta is closely associated with geochemistry of Nb. Since we had no Nb determination at our disposal, no conclusion could be made as concerns this pair of elements. According to Taylor (1965), the contents of Ta in arkoses and shales are 2 g . t^{-1}; the values determined by Gleeson and Boyle (1980) for shales of different types are analogous (Table 45, 46). The laboratory (Stráž pod Ralskem) for metabasites and for amphibolites established Ta values 5 to 10 times lower than average values given in the literature.

Scandium

In sediments, scandium occurs mainly in shales, clays, greywackes, and argillites in concentrations of 10—25 g . t^{-1}. This concentration range essentially agrees with average Sc contents in black slates of the Malé Karpaty crystalline complex. Exception to this finding are the anomalous low contents of REE in nime

Table 46

Ranges of variation and median of trace elements in the rocks from Keno Hill area. Adapted according to Gleeson — Boyle (1980)

Rock type No. of sample		Quartz-sericite schist 23	Quartzite 95	Phyllite 76	Greenstone 44
Cu	R M	2—32 4	2—400 2	2—180 4	2—2600 60
Pb	R M	2.5—145 2.5	5.2—1350 2.5	2.5—1800 2.5	2.5—65 2.5
Zn	R M	5—2200 70	5—8000 20	5—360 60	5—460 110
Ni	R M	2.5—240 10	2.5—130 2.5	2.5—95 20	2.5—145 70
Co	R M	2.5—40 2.5	2.5—20 2.5	2.5—55 2.5	2.5—60 10
As	R M	1—560 1	1—60 1	1—70 1	1—44 1
Sb	R M	0.5—1100 0.5	0.5—30 0.5	0.5—20 0.5	0.5—3.0 0.5
Mo	R M	0.5—15 0.5	0.5—9 0.5	0.5—20 0.5	0.5—3 0.5
W	R M	2 2	2 2	2 2	2 2
U	R M	0.4—4.6 2	0.1—6.7 1.5	0.8—13.5 2.5	0.4—4.6 2
Sn	R M	NDT—10 5	NDT—10 4	NDT—24 5	NDT—11 NDT
Ag	R M	NDT—0.5 NDT	NDT—7.6 NDT	NDT—1.2 NDT	NDT—1.2 NDT
F	R M	150—1430 350	ND—1825 180	ND—1500 550	70—1110 320
Ba	R M	324—6588 750	80—9461 350	277—14345 1200	82—9674 400

Explanations: R — range of variation; M — median. Contents in $g.t^{-1}$; NDT — not detectable.

samples from the productive zones (type A); the average value of Sc contents (34.4 g . t^{-1}) is higher than the concentration range mentioned above. There are no other exceptional Sc contents in individual areas and shale types. Only samples of the A type from the productive zones (31 samples — average 28.0 g . t^{-1}) exhibit a tendency to an increase in Sc contents with increasing organic matter. This fact has not yet been cleared up as there is little known on the geochemical behaviour of Sc. Possibly, a direct biochemical dependence of Sc on organic matter is involved, as it forms a trace admixture in marine organisms and plants and takes part in organic red-ox processes in them. An appreciable amount of Sc has also been found in peat, coal and oil. In coal ash from the Soviet Union up to 140 g . t^{-1} Sc has been asserted (V l a s o v, 1966 in F r o n d e l, 1970). The origin of Sc in coal is questionable; it can be bound to organo-metallic compounds or is adsorbed on organic substances from surface waters. The carbonaceous matter may thus act in sediments similarly as in accumulation of uranium. Such a bonding mechanism may also be considered for Sc in black slates of the Malé Karpaty crystalline complex. However, there have also been ascertained low Sc contents in the presence of organic matter. R o s s and R o s e n b a u m (1962 in F r o n d e l, 1970), for example, record the Sc content in oil shale only equal to 10 g . t^{-1}. In the paper of C a m b e l — S p i š i a k (1980) the contents of Sc determined with the use of the INAA and SPA methods are compared; the comparison has shown that neutron activation analysis gave higher values than the spectrochemical method, but the differences were quite small.

Hafnium

Hafnium is one of the elements the content of which in the rock depends on the content of zirconium, because its predominant part is accumulated in the mineral zircon. Therefore the Zr/Hf ratio is also characteristic and significant for individual rock types. In sediments it depends on the content of clastogenic or authigenic zircon in the mineral composition of rocks. The average contents of hafnium in the earth's crust range from 3 to 4.5 g . t^{-1}. Other elements accompanying increased Hf contents are Be, Cs, U, and partly praseodymium, samarium and gadolinium, tin and tantalum. The results presented here are essentially identical with the literary records. The Tables of element contents reveal that the rocks of productive zones (type A) have average Hf contents equal to 3.6—4.2 g . t^{-1}; the pyrite-bearing slates and sulphide ores (types B, C) only 2.9 g . t^{-1}, and heavy fractions of rocks (types B, C) only 0.9 g . t^{-1}. On the contrary, the slates outside the productive zones have an unusually high average Hf content 7.5 g . t^{-1}, and in the Harmónia Group 6.3 g . t^{-1}. The increased contents are due to a higher amount of zircon in rocks, which occurs in minor amounts in pyrite ores and sulphidic rocks. However, it is possible that the primary Hf/Zr ratio in zircons of different shale types differs.

Galium

The average value of gallium in the earth's crust is given as 17 g . t^{-1} (F a i r b r i d g e, 1972). The values for sedimentary rocks vary from 4 g . t^{-1} (carbona-

tes), through 12 g . t^{-1} (sandstones) and 20 g . t^{-1} (deep-sea sediments) to 25 g . t^{-1} (shales). In our Tables the Ga values in the Harmónia Group are 25.8 g . t^{-1}, in slates outside the productive zones 24.6 g . t^{-1}, in slates of productive zones 11.8 g . t^{-1} and in heavy fractions 8.4 g . t^{-1}.

The substantially decreased Ga contents in the black slates of productive zones in relation to the clayey-siliceous metamorphites outside the productive zones is regarded as a reasonable expression of the mineral composition of these rocks. Few determinations by the means of the SPA gave 22 g . t^{-1} as a mean of 10 analyses (Table 30), 39 g . t^{-1} for the gneisses from the Bratislava massif 39 g . t^{-1} Ga (5 samp.) and 15 g . t^{-1} for phyllites (3 samp.) (Table 31.) The values for 11 phyllite samples from the Pezinok—Pernek crystalline complex were 29 g . t^{-1}, and 25 g . t^{-1} for the phyllites of the Harmónia Group (8 samples). This comparison proves a relatively good accord between the INAA and SPA results.

Rubidium and cesium

Rubidium and cesium are geochemically important elements, which are bonded particularly to potassium-containing minerals. According to Taylor, the average contents of Rb and Cs in the earth's crust are in basalts 30 g . t^{-1} Rb and 1 g . t^{-1} Cs, in granites 150 g . t^{-1} Rb and 5 g . t^{-1} Cs, and in granodiorite 120 g . t^{-1} Rb and 2 g . t^{-1} Cs. Average values in various types of sedimentary schists are 140 g . t^{-1} Rb and 5 g . t^{-1} Cs; in arkoses 120 g . t^{-1} and 3 g . t^{-1} Cs; in quartzites 30 g . t^{-1} Rb and limestones 5 g . t^{-1} Rb.

The rubidium contents in Malé Karpaty slate samples, taken outside the productive zones (Table 40) are comparable to those of sedimentary slates referred to in the literature (123 g . t^{-1} Rb and 4.4 g . t^{-1} Cs). According to Table 41, the slates of the Harmónia Group have 168 g . t^{-1} Rb and 4.2 g . t^{-1} Cs. The slates from the productive zones of the Malé Karpaty (type A — Table 37 or types B, C — Table 38) have greatly varying contents of the two elements; the average values in the rocks of productive zones are 88 g . t^{-1} Rb and 2.2 g . t^{-1} Cs. The group of slates having anomalous chemistry gave only 44 g . t^{-1} Rb and 1.3 g . t^{-1} Cs (the slates belong to productive zones).

For lack of space, the causes of decrease in Rb and varying K/Rb ratio in slates from the productive zones and in slates with discernible pyrite will not be discussed thoroughly in this paper. The reasons have already been broadly mentioned in the section discussing the TR contents in the rocks. The comparison of the results obtained by the INAA method with the values of alkali contents determined by C a m b e l et al. (1981) with the use of flame photometry, has shown that in the phyllites or slates examined the Rb contents defined by the latter method range from 57 to 74 g . t^{-1} and the Cs amount from 1.6 to 2.6 g . t^{-1}. The INAA method used for the crystalline schists (biotite phyllites and gneisses) occurring outside the mineralized zones gave higher Rb values (123 g . t^{-1}) and Cs contents (4.4 g . t^{-1}) than the flame photometry and atomic absorption method. In slates of types B, C from the productive zones, the INAA gave 80 g . t^{-1} Rb and 1.8 g . t^{-1} Cs, i.e. approximately the same contents as determined by photometry in clayey-siliceous metamorphites.

It should be remarked that the two groups of results are within content li-

mits defined for Rb and Cs in sedimentary rocks, and that the results obtained photometrically have been confirmed by the method of atomic absorption.

In the last paper of Heinrich et al. (1980), the Rb content was stated for sedimentary rocks as 100 g . t^{-1}, ranging from 90 to 110 g . t^{-1}, and as 97 g . t^{-1} for metamorphites of the upper parts of the earth's crust. The value of Rb equal to 190 g . t^{-1} determined for dark and black shales of Germany is at variance with our results. One of the causes of such a great difference may be the fact that the Malé Karpaty were relatively intensely metamorphosed and the shales from Germany were metamorphosed to a lower degree or not at all.

Uranium and thorium

The interpretation based on the determination of U and Th contents by the three-component γ-spectrometric analysis is presented in part III. The results of measurements are listed in Tables of the catalogue. The results obtained by the neutron-activation analysis differ somewhat from the above results. The INAA data are tabulated in Chapter IV. Even a cursory comparison of the results shows that the γ-spectrometric method gives higher uranium values than the INAA method and only little different values for thorium, either a little lower (usually) or a little higher. Table 33 presents the average contents of U and Th in rocks divided into groups according to several criteria. The gamma-spectrometric analyses were made by RNDr. Kátlovský, CSc.

The comparison of arithmetic means of U and Th values (in rocks of not identical sets) obtained by γ-spectrometric and neutron activation analyses is given below (numbers in denominators = number of samples, numerals in parentheses = values obtained by INAA):

Productive zones,
slates of type A
Th = 3.07/36; (3.8/31)
U = 12.46/36; (7.4/31)
Heavy fractions, INAA: Th = 1.3/10
Slates outside productive zones
Th = 7.66/40; (7.4/18)
Th = 9.20/17; (9.8/16)

Productive zones,
slates of types B, C
Th = 3.58/26; (3.5/15)
U = 19.7/26; (6.8/15)
U = 11.2/10
Harmónia Group
U = 4.27/40; (3.1/18)
U = 4.30/17; (3.7/16)

The two methods applied brought very similar values of U and Th, especially for slates occurring outside the productive zones. The γ-spectrometric method gave widely differing values only for U in rocks of the productive zones in relation to those of the INAA, i.e. almost twice as high.

Moore and Swami (in Fairbridge, 1972) give the value of 12 g . t^{-1} Th for sedimentary rocks, which is evidently higher than the Th values in the Malé Karpaty slates.

There are more data on the uranium contents in different types of shales. For comparison some data of Wright (1972 in Encyclopedia of Geochemistry, Fairbridge, 1972) are cited here; uranium content in g . t^{-1}:

Black shales within a range of	3—250 g . t^{-1}	, median 8
red, grey and green shales	1.2—12	, median 3.2
limestones and dolomites	0.1—9	, median 2.2
bentonites	1—21	, median 5
thinly schistose metamorphites	1—6.4	, phyllites 1.0—2.7
amphibolites	2.6—41	gneisses 4.5—15

The comparison of our results with those cited above shows that the slates of productive zones have high U contents and decreased Th contents relative to the shales outside the productive zones.

IV.2. Comments on the contents of Au, Sb, As, Zn and Ag, as established by neutron activation analysis

These elements will be mentioned here only briefly, as they are discussed in Chapter III and in several special publications (Cambel — Strešk o — Škerenčáková, 1980; Cambel — Strešk o — Mičuda, 1981). It ought to be noted that the repeated INAA analyses (lab. Czechoslovak Uranium Industry, Stráž pod Ralskem) performed with new instruments of higher detectability limits, brought more precise results. The values for Au contents approached those obtained by atomic absorption method, if some anomalous values affecting the total average are omitted (we recommend to compare Table 34 a, b, c and Tables in this Chapter). The lowest Au contents are in slates outside the zones of mineralization (thousandths of g . t^{-1}) and in mineralized rocks to ores, or heavy fractions of these rocks (hundredths to thousandths of g . t^{-1}). Syngenetic pyrites are not concentrators of gold, which does not exceed the background value in them (Table 34).

Antimony

On the basis of new results, the antimony contents determined by the neutron activation analysis approached those obtained by atomic absorption procedure, particularly in the rocks outside the productive zones and in the Harmónia Group. Slates from the productive zones (types A, B and C) displayed much higher Sb values compared with those of the AAS method: type A — 27.94 g . t^{-1}, types B and C — 34.95 g . t^{-1}, and heavy fractions — 57.3 g . t^{-1}. According to AAS method, type A in productive zones — 22.6 g . t^{-1} Sb, and B, C types 25.3 g . t^{-1}, slates outside the zones (phyllites and gneisses) — 1.5 g . t^{-1}. These data are acceptable, if we realize that antimony deposits occur in these very zones. For comparison we present here some elements from the group of polymetals in graphitic phyllites or schists, from the paper of Gleeson and Boyle (1980) (Table 45). Average values of a major number of analysed rocks from the Keno Hill district, Yukon, are listed in Table 46. This area is suitable for comparison because its polymetallic mineralization is genetically analogous to that of the Malé Karpaty. In contrast to the Malé Karpaty the graphitic and mafic rocks in that region do not have anomalous concentrations

of Sb but they have neither antimony deposits. The average Sb content is 1.2 g . t^{-1} and As content is 2.5 g . t^{-1}. The mean Sb content for various shale types is 0.5 g . t^{-1} and 1 g . t^{-1} is the mean As content.

Arsenic

We do not regard the As contents given in our Tables as authoritative and acceptable as the values have not been checked against results of other analyses, and the data published elsewhere are widely different. The incorrectness of the data in also confirmed by the average values of the slates in Harmónia Group equal to 44 g . t^{-1}, the average in slates outside the productive zones being 6.1 g . t^{-1} (18 analyses) and 3.3 g . t^{-1} after excluding three anomalous contents. Irrespective of the questionable correctness of the individual results, the tendency to reduction of arsenic amount with increasing metamorphic grade (metamorphic recrystallization) is observable; this phenomenon was studied by Rösler et al., 1980.

The contents of arsenic in slates of type A from the productive zones reach very high values of 598.5 g . t^{-1}, higher than slates of types B and C (215 g . t^{-1}). The former value is caused by four high values (above 1300—6300 g . t^{-1}), which distort the result. It is to be stressed that the antimony ores of the Malé Karpaty have high arsenic contents and the increased gold contents are also associated with rich arsenopyrite occurrence. Therefore, these anomalously high As contents cannot be a-priori refuted. Pyrite accompanying the Sb mineralization in dark slates are also rich in As, which, however, is absent in pyrite of the syngenetic origin. These facts are a reason why the authors do not reject the high values of arsenic but think their correctness to be doubtful.

There are very few data on the arsenic contents in metamorphosed rocks. Onishi (1969 in Wedepohl, 1970) presented (Tables 33-M-1 and 33—0) the following values: in metapelites (phyllites, gneisses, amphibolites) 0.5 g . t^{-1} to 4 g . t^{-1}; for graphitic argillites and phyllites (29 samples) he cites Boyle's data from 1965 — 5 to 70 g . t^{-1} with average value of 18 g . t^{-1}, and for quartzitic rocks: 5 and 7 g . t^{-1}.

The reader is referred to Tables 45, 46. In Table 46 Boyle determined the mean As content as 1 g . t^{-1} and in Table 45 an average value from eight samples of graphitic phyllite as 2.5 g . t^{-1}. It is also recommended to take notice of Rösler's Table, 1980, published in our paper (Table 44). In conclusion it must be stated that arsenic is one of the elements that are difficult to identify analytically and the knowledge of which is scanty. Therefore, we have cited here even data that raise doubt of their correctness.

Zinc

The contents of zinc in the slaty rocks of the Malé Karpaty as determined by the method of atomic absorption are thought to correspond to reality. The average values of Zn contents in various rock types are given in Tables 34 and 35. The values are: 102.7 g . t^{-1} jointly for rocks types A,B,C of the productive zones (42 analyses); 90.3 g . t^{-1} for rocks of A type (27 analyses); 86.9 g . t^{-1}

for rocks outside the productive zones (26 analyses). The integrate average is 97.9 g . t^{-1} for 68 analyses. The average values obtained by neutron activation method are twice to three-times higher. According to G l e e s o n and B o y l e the mean Zn content for sericite-quartzose phyllites is 70 g . t^{-1}, 60 g . t^{-1} for phyllites, and 110 g . t^{-1} for greenschists. The average Zn in the earth's crust is 70 g . t^{-1} (F a i r b r i d g e, 1972).

Silver

The values of silver obtained by neutron activation method correspond in the order of magnitude to the data published by other authors and range from 1.3 to 1.6 g . t^{-1}. Its contents are below the detection limits of the INAA method.

Translated by H. Zárubová

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Review by Z. POUBA, J. ČADEK

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List of localities*

1. 1-OH.A Doľany, Kozárovský brook, sample from a bed with higher Si content. Dark-grey biotite phyllite.
2. 2-OH.A Borinka village, Black folded slate in a complex of amphibolites and phyllites. Svätý vrch.
3. 3-OH.A Lošonec village, borehole no. 9, 44—44.6 m. Dark-grey schistose phyllite.
4. 4-OH.A Horné Orešany, dark-grey biotite phyllite. Meďná el. points 334 and 314, S of Slapý vrch hill.
5. 5-OH.A Pezinok — Rybníček, Hrubý vrch, western slope between el. points 479 and 476. Dark-grey quartz-biotite slate.
6. 6-OH.B Cajla, Pezinok, Hrubá dolina; gallery opposite to Michal gallery. Light grey sericite-chlorite slate.
7. 7-OH.A Pezinok deposit, Kolárska gallery, left of meas. point 4. Dark sericite-chlorite phyllite with antimonite.
8. 8-OH.A Modra-Harmónia, Dolinkovský vrch, el. point 391. Dark to black phyllite with biotite porphyroblasts.
9. 9-OH.A Pezinok, 250 m S of the bathing pool. Weathered black biotite schist.
10. 10-OH.A Pezinok, Ferdinand gallery, dark-grey quartz-biotite phyllite.
11. K-1.A Modra-Harmónia, spotted slates of the Harmónia Group, quarry near the dam in the Kamenný brook valley.
12. K-3.A Mariánka village, quarry, Toarcian (Jurassic), Mariatal shale.
13. K-4.A Pernek, beside the house no. 232. Mariatal shale (Toarcian).
14. K-5.A Pezinok, Hrubá dolina, pit heap of the Zlatá gallery (near the chalet Koliba). Greyish-black fine-grained sericite-chlorite slate.
15. K-6.A Dubová village, game-keeper's Fúgeľka; water reservoir about the new chalet. Spotted slate of the Harmónia Group.
16. K-7.A Pezinok, Hrubá dolina, 400 m W of Kablo chalet. Biotite-sericite phyllite with segregation quartz veins.
17. K-9.A Dubová village, Fúgeľka, game-keeper's cottage, road cutting, ca. 300 m above the new building. Quartz-sericite slate (probably Permian).
18. K-10.A Dubová, Fúgeľka game-keeper's cottage, road from the new building. Black slate (probably Permian).
19. K-12.A Modra-Harmónia, lower limestone quarry. Fine-grained biotite-sericite slate (Harmónia Group).
20. K-13.A Pezinok, Hrubá dolina, the large limestone quarry, W of the brook. Dark to black rock with streaks of organogenic pigment.
21. K-16.B Pezinok, pit-heap of Augustin gallery. Black carbonaceous slate with quartz.
22. K-17.B Bratislava, road below Devín Castle, exposure near the monument. Sericite phyllite with crumpled mica minerals.
23. K-18.A Bratislava, crematorium, road to the quarry below the forest. Black slate with quartz and traces of oxides.
24. K-19.A Bratislava, quarry near the crematorium. Dark-grey biotite slate with quartz veinlets and sulphide streaks.
25. K-20.B Kuchyňa village, above Puklišova gallery, pit heaps above the brook. Biotite phyllite.
26. K-21.A Kuchyňa — Modranská dolina, hill above the gallery. Quartz-sericite-biotite phyllite with layers of quartz granoblasts.
27. K-22.A Pezinok — Rybníček, on the ridge 20 m SE of Gajdoš hill. Siliceous dark slate with porphyroblast of muscovite and biotite.
28. K-23.A Horné Orešany, field at the outskirst of the village. Highly siliceous biotite phyllite.

* The terms "graphitic quartz — graphite — sulphide ore" are taken from the literature on the rocks of the Malé Karpaty. As these rocks do not contain graphite but an organic substance of anthracitic character they are written in inverted commas.

29. K-24.A NE of Doľany, cutting of the road to the hill top. Muscovite-biotite micaschist-phyllite with relics of clastic feldspars and quartz.
30. K-25.B Pernek, old pit-heap below Misársky Ostrobec. Highly siliceous black slate.
31. K-26.A Modra-Harmónia, Dolinkovský vrch, W of No. 382. Light-grey biotite hornfels with biotite and muscovite.
32. K-27.A Záhorská Bystrica, quarry near the working youth's hostel. Biotite phyllite (Harmónia Group?).
phyllite, slightly spotted (Harmónia Group).
33. K-28.A Bratislava, highroad Lamač-glass works, 300 m N of the viaduct. Micaschist-phyllite with garnets.
34. K-29.A Bratislava, highroad Lamač—Dev. Nová Ves, outcrop at the railway. Biotite phyllite to gneiss.
35. K-30.A Pezinok — road across the vineyards on Malá homola hill. Biotite
36. K-31.A Častá quarry. Dark quartz-biotite-muscovite phyllite. Častianska dolina.
37. K-32.A Častá, border of the row of gardens along the road to the castle. Biotite phyllite with a major amount of carbonaceous pigment.
38. 1 C. A Crematorium, exposure. Dark siliceous rock (bituminous quartzite).
39. 2 A Bratislava — Dúbravka, glass works, artificial exposure 100 m before the cross-roads. Quartz phyllite with little biotite.
40. 3 A Bratislava — Dúbravka, artificial exposure in front of the glass works, 50 m before the bridge-over. Dark biotite phyllite.
41. 4 A Kuchyňa — Modranská dolina, 500 m from the cottage on the slope above the road. Massive, dark siliceous slate.
42. 5 A Kuchyňa — Modranská dolina, near the forest lodge on the slope, 500 m above the road. Dark siliceous slate.
43. 6 B Kuchyňa — Modranská dolina, at the lower pit heap below the Puklišova gallery, 300 m to the right. Dark siliceous slate.
44. 7 B Kuchyňa — Modranská dolina, entry to a little gallery below the Puklišova gallery. Dark slate with biotite and sulphides.
45. 8 B Kuchyňa — Modranská dolina, middle pit heap below the Puklišova gallery. Biotite micaschist-phyllite with garnets.
46. 9 B Kuchyňa — Modranská dolina, pit heap of the Puklišova gallery. Dark siliceous slate.
47. 10 B Kuchyňa — Modranská dolina, a small pit heap on the right bank of the brook, between the cottages. Dark siliceous slate.
48. 11 B Kuchyňa — Modranská dolina, entry to a little gallery between the cottages. Dark siliceous slate.
49. 12 B Kuchyňa — Modranská dolina, at the little gallery between the cottages, on the right bank of the brook. Dark siliceous slate.
50. 13 B Kuchyňa — Modranská dolina, mid-slope at elev. point 544, on the right bank of the brook. Dark siliceous slate with some sulphides.
51. 14 B Kuchyňa — Modranská dolina, outcrop in the brook bed, ca. 100 m from the little gallery. Dark-grey siliceous slate with some biotite.
52. 15 B Pernek — Pernecká dolina, first pit heap from Pernek (Zubau gallery). Dark siliceous slate.
53. 16 B Pernecká dolina, first pit heap from Pernek (Zubau gallery), black slate on the pit heap.
54. 17 B Modra — Harmónia, lower limestone quarry on the road to Dolinkovský vrch. Dark phyllite with weathered-out sulphides.
55. 18 B Modra — Harmónia, upper limestone quarry. Dark sericite-chlorite phyllite with sulphides and carbonaceous pigment.
56. 19 A Dubová, Fúgeľka, 100 m above the pioneers' camp. Dark sericite-chlorite phyllite.
57. 20 A Dubová, above the church. Dark-grey biotite phyllite.
58. 21 A Častá, at the end of the village, at the road to Červený kameň, near the chapel. Dark-grey phyllite.
59. 22 A Častá, Sivá baňa, outcrop in the opening of the gallery. Black sericite phyllite.

60. 23 A Častá, Častianska dolina, large quarry. Dark quartz-sericite-chlorite phyllite with biotite.
61. 24 A Častianska dolina, near the spring between the junction of brooks above the game-keeper's lodge. Grey phyllite of transitional type (more detrital).
62. 25 A Pezinok — Cajla, path along the ridge to Malá Cajlanská homola, on the forest edge. Grey quartz phyllite.
63. 26 A Dolany, above the church, ca. 500 m from the vineyard. Dark-grey quartz-biotite phyllite.
64. 27 A Pezinok, closure of the Rybníček valley, a trench. Black quartzitic slate.
65. 28 A Pezinok, E of Čertov kopec, PH gallery. Siliceous slate with tuffaceous material.
66. 29 C Rybníček, pit heap of Ján III gallery. Amphibolite-sulphide ore.
67. 30 B Rybníček, bank of the brook at the closure of the valley. Weathered siliceous slate.
68. 31 A Pezinok — Cajla, Sb ore mine works. Pyrite gallery. Micaschist--phyllite with biotite.
69. 32 C Pezinok, pit heap of "horná Augustín" gallery. Quartz-graphite ore.
70. 33 C Pezinok, pit heap of Čmele I. gallery. Sulphidic quartz-"graphite" ore.
71. 34 B Pezinok, pit heap of Čmele II. gallery. Sulphidic quartz-"graphite" ore.
72. 35 A Pezinok, pit heap of Čmele III. gallery. Spotted amphibolite.
73. 36 A Pernek, Misársky Ostrobec, below the "dolná Karol" gallery. Biotite micaschist-phyllite.
74. 37 A Misársky Ostrobec, bank of the brook below the "dolná Karol" gallery. Biotite micaschist-phyllite.
75. 38 A Mariánka village, large quarry. Dark quartz-sericite-chlorite slate (diaphthorite).
76. 39 A Mariánka, bank of the brook, above the large quarry, beside the cottages. Grey diaphthorized quartzite-phyllite.
77. 40 B Pernek, pit heap of the "horná Karol" gallery. Strongly mineralized sulphidic quartz-"graphite" rock.
78. 41 A Pernek, pit heap of the "horná Karol" gallery. Dark graphitic quartzite-phyllite with amphibole.
79. 42 B Pernek, pit heap of the "dolná Karol" gallery. Sulphidic quartz--"graphite" ore.
80. 43 C Pernek, pit heap of the „dolná Karol" gallery. Sulphidic quartz-" graphite" ore.
81. 44 A Pernek, pit heap of the "dolná Karol" gallery. Dark-grey biotite phyllite.
82. 45 A Pezinok, pit heap of the Ján III gallery. Actinolite schist.
83. 46 B Pezinok, pit heap of the Ján III gallery. Pyritized quartz-graphite rock.
84. 47 C Pezinok, pit heap of the Ján III gallery. Sulphidic quartz-"graphite" ore.
85. 48 B Pezinok, pit heap of the Ján III gallery. Sulphidic ore with amphibole + quartz.
86. 49 A Pezinok, pit heap of the Ján III gallery. Mineralized carbonatized amphibolite.
87. 50 A Pezinok, pit heap of the Ján I gallery. Hydrothermally altered pyritized carbonatized slate.
88. 51 A Pernek ore district, the uppermost pit heap in the valley. Hydrothermally altered dark slate.
89. 52 B Pernek ore district, the uppermost pit heap in the valley. Metatuff with pyrite.
90. 53 B Pezinok, pit heap of the "horná Augustín" gallery. Sulphidic quartz--"graphite" ore.

91. 54 A Fezinok, pit heap of the "horná Augustín" gallery. Black phyllite with veinlets of segregation quartz.
92. 55 C Fezinok, pit heap of the "horná Augustín" gallery. Sulphidic ore with amphibole + quartz.
93. 56 A Pernek, pit heap of the "horná Augustín" gallery. Quartz-"graphite" phyllite with amphibole and biotite.
94. 57 A Pezinok—Cajla, road cutting at the water reservoir near the game--keeper's lodge (area of the hospital). Quartz-"graphite" phyllite with pyroclasts and weathered-out sulphides.
95. 58 A Pezinok-Cajla, road to Kolársky vrch, 100 m from the game-keeper's lodge. Ditto as in 94.
96. 59 A Pezinok, Sb-deposit, locality not strictly determined. Schistose mylonite, hydrothermally altered.
97. 60 A Pezinok, Ore mine works. Dark slate from exploration galleries. Quartzite phyllite.
98. 61 A Pezinok—Rybníček, cutting of the road to Köberling. Quartz-graphite--biotite phyllite.
99. 62 A Pezinok—Cajla, pit to the right of the road, NW of the game-keeper's lodge. Corrugated black phyllite.
100. 67 A Pezinok, Kolársky vrch, borehole KV-3, 130—131 m. Black slate.
101. 68 A Pezinok, Kolársky vrch, borehole KV-1, 217—221 m. Folded black phyllite.
102. 69 A Pezinok, Kolársky vrch, borehole KV-5, 104.6 m. Micaschist-phyllite with well developed biotite.
103. 70 B Pezinok, Kolársky vrch, borehole KV-3, 203—218 m. Folded, highly carbonatized black phyllite.
104. 71 C Fezinok, Kolársky vrch, borehole KV-4, 170.5 m. Carbonatized ore, hydrothermally altered.
105. 82 B Pezinok, Kolársky vrch, borehole KV-14, 75—80 m. Dark fine-grained phyllite with coarser-grained layers.
106. 83 B Pezinok, Kolársky vrch, borehole KV-15, 90—105 m. Dark slate with visible sulphides.
107. 84 B Pezinok, Kolársky vrch, borehole KV-16, 78—88 m. Black phyllitized meta-arkose.
108. 85 A Pezinok, Kolársky vrch, borehole KV-18, 83—91 m. Quartzite-phyllite with pyroclasts.
109. 86 A Pezinok, Kolársky vrch, borehole KV-18, 242—248 m. Corrugated black phyllite.
110. 87 A Pezinok, Ore mines, drift entry in Sb-gallery, heading, gallery NW of meas. point 174. Folded dark slate.
111. 88 A Pezinok, Sb-gallery; NW of meas, point 12. Folded "quartz-"graphite" phyllite.
112. 89 C Pezinok — Hrubá dolina, opening of the Rýhová gallery. Sulphidic quartz-"graphite" ore.
113. 90 A Pezinok — Hrubá dolina, big limestone quarry, its first part. Dark folded phyllite (probably Harmónia Group).
114. 91 A Pezinok — Hrubá dolina, big limestone quarry. A layer of dark to black calcareous slate (probably Triassic).
115. 92 A Dubová, ca. 600 m below the Fúgeľka game-keeper's lodge, new vineyards at the outskirts of the village. Carbonatized pyroclastic rock — black phyllite (Harmónia Group).
116. 93 A Dubová, new vineyards at the outskirst of the village, ca. 600 m below the game-keeper's lodge. Black phyllite.
117. 94 A Častá village, Kukla hill, about 400 m E of el. point 564. Folded black phyllite.
118. 95 A Dubová village, opposite to the game-keeper's lodge Fúgeľka. Dark--grey spotted slate with biotite.
119. 96 A Dubová, Fúgeľka, road into the wood, towards the quartzite complex. Dark phyllitic slate (Harmónia Group).
120. 97 A Pezinok, old Rybníček gallery. Highly quartzose "graphitic" slate.

121. 98 A Pezinok, road-cutting some 1000 m below the old Rybníček gallery. Black quartzose slate.
122. 99 A Pezinok, the new Rybníček II gallery. Siliceous black slate.
123. 100 A Pezinok, the new Rybníček I gallery. Black quartz phyllite with amphibole relicts.
124. 101 A Pezinok, Rybníček, Hrubý Ostrý, foot of the slope, 250 m from the bridge. Metapyroclastic rock-amphibolite.
125. 102 A Pezinok, Koňské Hlavy, the Rudolf gallery. Corrugated phyllite to biotite mica-schist.
126. 103 A Pezinok, Veľká Cajlanská homola. Diaphthorized mica-schist-phyllite.
127. 104 A Pernek, trench ca. 400 m behind the Zubau gallery, on the left bank of the brook. Amphibolite.
128. 105 A Pezinok, Cajlanská Hrubá dolina, upper part of the large quarry. Dark phyllite (Harmónia Group).
129. 106 A Pezinok — Cajla, road cutting above the hospital. Mica-schist-phyllite with biotite and pyroclasts.
130. 107 A Píla — Rúbanica, 50 m S of el. point 299.8. Biotite phyllite.
131. 108 A Cajlanská dolina, large quarry. Dark weathered quartzite phyllite (probably Harmónia Group).
132. 109 A Dubová village, water reservoir. Biotite phyllite.
133. 110 A Dubová, el. point 312, 1 km NW of the village. Dark quartz phyllite showing initial biotitization.
134. 111 A Bratislava—Rača, Malý Javorník, 800 m NE of the el. point. Fine-grained dark-grey phyllite.
135. 112 A SE of Borinka, 500 m S of el. point 368. Light-grey phyllitic biotite slate.
136. 113 A Veľké Tŕnie, W of Solčár, 250 m E of el. point 268. Dark phyllitic sericite slate.
137. 114 B Veľké Tŕnie, 250 m E of el. point 161, road above the highway. Dark slate with a little pyrite.
138. 115 B Pezinok, Ore mines, Šimon crosscut in Sb-gallery, 22 m E of meas. point 7. Black slate. Sample from the collection of J. Chrappa.
139. 116 B Pezinok, Sb-gallery, Šimon crosscut, meas. point 6. "Graphite"-sericite phyllite with antimonite impregnation. Sample from the collection of J. Chrappa.
140. 117 A Pezinok, Ore mines, Kolárska 2 gallery. Black phyllite at the contact with granite. Sample from the collection of J. Chrappa.
141. 118 A Pezinok, Sb-gallery, Šimon crosscut, 44 m from meas. point 7. Black phyllite. Sample from the collection of J. Chrappa.
142. 119 A Pezinok, Ore mines, Kolárska 2 gallery, 3 m from crossing no. 5. Dark quartz-sericite phyllite. Sample from the collection of J. Chrappa.
143. 120 A Kuchyňa, Modranský brook, valley E of woodcutter's hut. Dark-grey biotite phyllite.
144. 121 A W of Kukla, between Králová and Píla. Dark slate, Harmónia Group.
145. 122 A Častá — Píla, S of Píla, 750 m SE of el. point 377, top of the ridge. Dark bituminous slate.
146. 123 A Kuchyňa — Modranská dolina, 350 m SE of woodcutter's hut, summit road to el. point 541. Dark quartz phyllite with biotite.
147. 124 B Pernek area, Lower gallery below Misársky. Dark mineralized bituminous slate.
148. 125 A Horné Orešany, exposure at the outskirts of the village on the roadside near the chapel. Biotite phyllite partly diaphthorized.
149. 126 A Doľany, 500 m E of el. point Klokočina, at the altitude of ca. 450 m. Dark slate (Harmónia Group).
150. 127 A Pezinok — Sb deposit, western margin of the lensshaped body. Biotite mica-schist.
151. 128 A Dolné Orešany, Maruša. Dark fine-grained biotite phyllite.
152. 129 A N of Doľany, Šišorétne, game-keeper's lodge below el. point 424, road cutting. Dark slate of the Harmónia slate.

153. 130 A Dúbravka, 50 m from the cliff Hlavice. Biotite phyllite.
154. 131 A Dolné Orešany, Kosa. Trench at the roadside. Dark phyllite, almost devoid of biotite.
155. 132 A Doľany, 1250 m N of the community. Dark-grey fine-grained phyllite, initial stage of biotitization.
156. 133 A Borinka, road to Santóberg, 500 m S of the mill. Dark-grey fine-grained phyllite, initial stage of biotitization.
157. 134 A Častá — Prašnice area. Dark phyllite with relics of clastogenic minerals and initial development of biotite (Harmónia Group).
158. 135 A Bratislava — Železná studnička, 1500 m SE of el. point 345. Dark, fine-grained quartz-biotite phyllite.
159. 136 A Harmónia — Kamenný brook, 125 m W of el. point 456. Dark spotted slate.
160. 137 B Cajla — Rybníček, below el. point 653, ore zone 200 m to the S along the ridge. Low-mineralized dark biotite phyllite.
161. 138 A Lamač, quarry at the crematorium. Dark paragneiss.
162. 139 A Pezinok — Baba, Koňské Hlavy, 250 m N of el. point 653. Dark biotite phyllite.
163. 140 A Doľany — Doľanská dolina, at the woodcutter's hut. Dark-grey fine-grained slate, Harmónia Group.
164. 141 A Limbach village, N of el. point 565, near the summit of Somársky vrch. Dark-grey phyllite, almost without biotite.
165. 142 A Pezinok, Ferdinand gallery, near meas. point 13. Black carbonatized slate with a small amount of pyroclasts.
166. 143 B Pernek — Zubau gallery, near meas. point 213. Dark slightly mineralized metasediment.
167. 144 A Limbach, N of el. point 565, northern slope of Somársky vrch. Dark-grey phyllitic biotite slate.
168. 145 A Častá — Prašnica, 500 m to the N. Dark metasediment.
169. 146 B Bratislava, Hrubý Pleš. Dark pyritized slate of B type, the second sample is dark biotite phyllite; the two types evaluated together.
170. 147 A Častá — NE of the quarry in Častianska dolina; crest of the hill on which there are metasomatites. Dark phyllitic slate.
171. 148 A Pernek, upper Pavol gallery, sample MH 2. Dark fine-grained phyllitic slate.
172. 149 A Kubalová, 500 m N of el. point 535. Dark slate.
173. 150 A Pezinok, Cajlanská dolina, sanatorium; pit heaps of Zlatá gallery. Dark slate of Harmónia type.
174. 151 A Borinka, Volhovisko, 500 m to the N. Fine-grained biotite phyllite.
175. 152 A W of Doľany, Zrkadlisko Hill, horizontal road along the border of the wood. Dark phyllitic slate.
176. 153 B Kuchyňa, Modranská dolina, gallery in Hlavná dolina below the woodcutter's hut. Strongly pyritized dark slate.
177. 154 A Cajlanská dolina, valley NW of the limestone quarry on Baba — underlying complex. Dark-grey quartz-biotite phyllite.
178. 155 A Jabloňové, Turecký vrch, cutting of the new road near el. point 488. Dark-grey fine-grained phyllite with little biotite.
179. 156 A Dubová — wood; W of the village hornfels occurrence. Dark slate of the Harmónia Group.
180. 157 B Jabloňové, Turecký vrch, borehole TV 2, depth 16.25 m, area of mineralization. Dark siliceous slate with pyrite.
181. 158 A Bratislava — Dúbravka, road to glass works, cutting, 300 m N of the viaduct. Dark, slightly biotitized phyllite.
182. 159 B Kuchyňa area, 200 m N of Gajdoš. Dark, slightly mineralized phyllitic slate.
183. 160 A Častá, cutting of the road leading to the NE of the quarry. Dark slate.
184. 161 A Bratislava, excavation for the crematorium. Bituminous quartzose slate.
185. 162 B Bratislava, crematorium, road to the quarry. Black quartzose phyllitic slate.

186. 163 A Modra — Harmónia, Dolinkovský vrch — lydite. Dark slate of the Harmónia type.
187. 175 A Pezinok, Kolársky vrch, borehole KV-21, depth 576 m. Harmónia Group. Dark slate.
188. 176 B Pezinok, Kolársky vrch, borehole KV-11A, depth 479 m. Dark slate.
189. 177 B Pezinok, Kolársky vrch, borehole KV-24, depth 482—483 m. Dark slate. Harmónia Group.
190. 178 B Pezinok, Kolársky vrch, borehole KV-11A, depth 479—489 m. Dark slate.
191. 164 A Pezinok, Pyrite gallery, drift entry to SE, meas. point 78. Dark slate.
192. 165 B Pezinok, Pyrite gallery, drift entry to SE, at polygonal point 8. "Graphitic" slate.
193. 166 A Pezinok, Pyrite gallery, crosscut at meas. point 78. "Graphitic" slate.
194. 167 B Pezinok, Pyrite gallery 2; 40 m from polygonal point 73. "Graphitic" slate.
195. 168 A Pezinok, Pyrite gallery, 50 m from the drift entry to SE. "Graphitic" slate.
196. 169 B Pezinok, Pyrite gallery, heading, 35 m from point 78. "Graphitic" slate.
197. 170 A Pezinok, Pyrite gallery, crosscut to SW at polygonal point 80. "Graphitic" slate.
198. 171 A Pezinok, Pyrite gallery, crosscut to NE, 10 from polygonal point 73. "Graphitic" slate.
199. 172 A Pezinok, Pyrite gallery, crosscut to SW, polygonal point 80. "Graphitic" slate.
200. 173 A Pezinok, Pyrite gallery, crosscut to SW, 10 m from polygonal point 80. "Graphitic" slate.
201. 174 A Pezinok, Kolársky vrch, borehole KV-12, depth 51 m. "Graphitic" slate.
202. 24 63-JV Harmónia, middle large quarry in the Kamenný potok valley. Spotted hornfels-phyllite with biotite.
203. 11-C Lower limestone quarry in Harmónia. Dark (overlying) shales.
204. KV-43 423 Pezinok, Kolársky vrch, borehole KV-43, depth 423 m. "Graphitic" slate.
205. 183 B Pezinok, Kolársky vrch, borehole KV-43, depth 398—402 m. Dark slate with sulphides.
206. 184 A Pezinok, Kolársky vrch, borehole KV-43, depth 406—409 m. Dark slate.
207. 30 63-JV Častá, pit heap of Sivá mine. "Graphitic" phyllite.
208. 52 63-JV Častá, vicinity of metasomatites in Častianska dolina. Biotite phyllite.

Catalogue of analyses

No.	Sample number	B	V	Cu	Ni	Co	Cr	Ba	Sr	Ti	Zr	C_{org}	Th	U	K	O	Si	Na	Al	Fe	M_g	Group number
1.	1 — OH A	39	159	42	45	3	81	12000	52.5	4800	129	1.17										2, 5, 7, 9, 15, 18, 20
2.	2 — OH A	36	690	148	30.9	3	76	890	10	3400	102	7.10										3, 5, 7, 9, 12, 17, 20, 25, 26
3.	3 — OH A	104	115	166	38	13.2	65	251	93	5100	100	1.27										2, 4, 6, 9, 19, 20, 32
4.	4 — OH A	0	159	60	42	3	95.5	710	110	6500	138	1.16										2, 5, 7, 9, 16, 17, 19, 20, 26
5.	5 — OH A	0	102	11.7	39	3	69	1070	141	4700	117	0.52										2, 5, 7, 9, 14, 17, 20, 26
6.	6 — OH B	35	117	18.2	37	3	74	12000	115	5400	79	0.78										2, 4, 7, 10, 15, 18, 21, 27, 32
7.	7 — OH A	10	209	8.7	110	3	50	182	141	525	20	5.81										3, 5, 6, 9, 17, 20, 28
8.	8 — OH A	35.5	720	5.1	14.1	3	34	370	15	890	20	13.92										3, 4, 7, 9, 15, 18, 20, 28
9.	9 — OH A	30.9	540	3.6	5.8	3	48	12000	71	3020	145	13.50										3, 5, 7, 9, 14, 17, 20, 24, 27
10.	10 — OH A	10	79	23.9	49	3	66	355	269	5100	51	0.99				46.91	27.76	3.64	8.44	4.27	1.45	2, 5, 7, 9, 13, 17, 20, 26, 32, 13a
11.	K — 1 A	41	120	30.9	45	3	78	575	100	6200	151	0.11				48.43	24.62	2.22	9.89	5.58	1.27	1, 5, 6, 9, 15, 18, 21, 26
12.	K — 3 A	37	57.5	30.2	41	3	42	195	1950	3900	107	0.47	7.1	2.0	1.34	48.87	16.16	0.56	5.53	2.82	1.55	1, 5, 6, 9, 12, 17, 21, 28
13.	K — 4 A	3	35.5	17	19.1	0	20.9	83	910	1590	36	0.46				45.33	13.18	0.20	1.93	0.65	0.27	2, 5, 6, 9, 14, 17, 21
14.	K — 5 A	0	60	39	33	3	60	300	182	3500	62	0.66	6.1	2.1	1.99	45.27	14.31	1.17	5.03	2.59	5.78	2, 5, 6, 9, 14, 17, 21, 26
15.	K — 6 A	45	69	32	43	3	49	295	91	4900	148	0.21	8.6	3.4	1.76	49.19	28.26	1.86	6.00	3.47	1.42	1, 5, 6, 9, 15, 18, 20, 26
16.	K — 7 A	3	83	48	17.8	1	117	12000	123	5400	170	0.27				49.68	30.53	1.64	7.27	3.50	1.29	1, 5, 6, 9, 14, 17, 20, 26
17.	K — 9 A	35.5	660	76	46	3	104	12000	98	5250	174	3.82				42.79	25.28	0	7.43	3.24	2.17	3, 4, 7, 9, 15, 18, 21, 26
18.	K — 10 A	36	630	56	35.5	3	95.5	12000	133	7900	174	2.82	10.7	8.4	4.70	45.68	26.44	0	7.16	4.30	2.08	2, 5, 6, 9, 15, 18, 21
19.	K — 12 A	37	288	100	15.5	0	141	12000	166	6900	155	4.93	11.6	5.3	4.24	48.76	26.47	1.33	7.42	2.78	1.64	3, 5, 6, 9, 15, 18, 21, 26
20.	K — 13 A	10	38	8.3	17.8	3	20.9	245	275	1200	20	0.64	2.8	3.8	0.88	51.53	5.32	0.08	1.95	1.16	10.30	2, 5, 6, 9, 15, 18, 21, 28
21.	K — 16 B	3	1120	98	355	15.9	102	12000	30	1950	151	4.94	1.4	43.3	1.44	40.06	28.31	0.22	2.69	8.71	0.09	3, 4, 6, 10, 13, 17, 20, 26, 13 b
22.	K — 17 B	74	132	30.9	49	11.7	83	955	45	5900	155	0.03	7.4	3.4	3.43	45.87	25.10	0.80	9.01	5.48	1.92	1, 5, 6, 10, 12, 17, 21
23.	K — 18 A	32	170	12	9.1	0	20.9	12000	148	3800	245	1.42	7.4	6.2	2.05	52.64	33.67	2.36	7.01	1.14	0.07	2, 5, 6, 9, 12, 17, 20, 26
24.	K — 19 A	0	110	76	18.6	3	74	1020	219	4800	126	0.28	9.1	3.1	2.13	51.54	29.22	3.16	8.68	3.54	1.45	1, 5, 6, 9, 12, 17, 20, 26
25.	K — 20 B	0	166	257	251	21.9	93	620	590	12000	200	0.38				40.23	21.19	3.60	8.80	7.35	2.83	1, 5, 6, 10, 14, 17, 21, 26
26.	K — 21 A	3	830	66	330	52.5	300	12000	182	7900	170	1.34				42.31	25.76	1.32	6.19	5.67	2.16	2, 5, 6, 9, 14, 17, 21, 26
27.	K — 22 A	3	360	10.4	7.6	0	38	12000	148	4800	145	4.10				46.71	30.91	4.04	8.34	0.84	0	3, 5, 6, 9, 14, 17, 20, 26
28.	K — 23 A	0	132	6.8	26.9	3	57.5	12000	320	5100	282	0.12				47.22	25.58	2.31	10.82	3.60	1.43	1, 5, 6, 9, 16, 19, 21, 26
29.	K — 24 A	30.9	102	16.6	30.9	3	25.1	12000	69	5750	269	0.19				49.36	27.66	1.26	9.89	5.15	1.72	1, 5, 6, 9, 15, 18, 20, 26
30.	K — 25 B	39	6000	7.9	14.8	0	1200	12000	15	4400	214	8.28				41.93	28.62	0.05	5.76	0.74	0.79	3, 4, 6, 10, 14, 17, 20, 26
31.	K — 26 A	46	95,5	123	44	3	74	12000	69	5750	115	0.98				49.06	31.10	1.13	7.59	4.42	1.28	2, 5, 7, 9, 15, 18, 20, 26
32.	K — 27 A	33	93	15.9	38	3	85	810	209	6800	132	0.07				52.44	27.93	2.37	8.64	3.47	1.61	1, 5, 7, 9, 12, 17, 20, 26
33.	K — 28 A	3	87	18.2	41	3	78	955	24.5	5100	102	0.03				50.25	29.62	2.17	8.11	4.05	1.21	1, 5, 7, 9, 12, 17, 20, 26
34.	K — 29 A	3	126	27	51	10.7	85	720	263	5500	141	0.07				43.99	25.04	1.93	10.57	5.56	1.94	1, 5, 7, 9, 12, 17, 21, 26
35.	K — 30 A	0	42	8.3	17.4	3	39	234	740	2690	44	0.20				48.36	15.88	1.05	4.27	1.76	0.86	1, 5, 6, 9, 14, 17, 21, 26
36.	K — 31 A	3	87	26.9	23.4	3	47	525	263	3800	112	0.24				51.50	31.99	2.96	6.86	3.19	0.83	1, 5, 6, 9, 15, 18, 20, 26
37.	K — 32 A	0	115	21.4	33	3	89	239	115	5000	155	0.30				48.34	28.55	2.77	8.47	4.66	1.51	1, 5, 6, 9, 15, 18, 20, 26
38.	1 C	0	214	1350	1860	65	26.3	38	30	410	191	1.19	1.4	9.7	0.12	29.26	6.7	0.4	0.5	30.8	0.05	2, 5, 11, 12, 17, 21, 27
39.	2 A	3	110	48	28.8	3	117	1000	340	5750	83	0.19	7.0	1.7	1.87	45.91	25.8	3.2	10.1	3.7	1.28	1, 4, 5, 7, 9, 12, 17, 21, 26
40.	3 A	57	117	30.9	28.8	3	79	680	224	5250	95,5	0.37	6.2	1.9	1.83	45.49	28.1	2.6	8.4	4.7	1.27	3, 4, 7, 9, 12, 17, 20, 26
41.	4 A	46	85	23.9	21.4	3	76	12000	282	3500	37	0.77	6.5	0.7	0.48	48.54	33.1	3.0	6.4	1.0	1.04	2, 5, 7, 9, 13, 17, 20, 24, 27, 13a
42.	5 A	44	850	24.5	10.2	3	316	870	141	5900	63	2.13										2, 5, 7, 9, 13, 17, 21, 24, 27, 13a
43.	6 B	54	1260	120	102	3	132	12000	59	3900	120	4.61				45.38	34.69	0.57	4.14	2.50	0.73	3, 5, 7, 10, 13, 17, 20, 24, 27, 13b
44.	7 B	3	166	159	159	18.6	141	12000	151	6300	63	2.21	7.9	2.8	2.60	41.85	22.70	2.9	8.8	4.6	2.9	2, 5, 7, 10, 13, 17, 21, 26, 27, 13b
45.	8 B	3	93	115	66	14.5	93	780	182	5600	57.5	1.13	6.1	3.1	0.17	45.93	26.7	3.1	9.4	4.9	2.42	2, 5, 7, 10, 13, 17, 21, 26, 27, 13b
46.	9 B	269	181	81	76	12.6	110	12000	162	5500	57.5	0.61	5.3	3.9	3.48	45.38	25.14	0.11	8.70	3.66	0.69	2, 5, 7, 10, 13, 17, 21, 27, 13b
47.	10 B	78	870	191	112	11.2	72	12000	141	4900	141	0.38	3.5	9.7								1, 4, 7, 10, 13, 17, 21, 13b
48.	11 B	42	132	229	117	23.4	110	600	234	4900	100	0.40	11.1	3.8	0.50	48.23	28.45	4.16	6.99	2.91	0.85	1, 4, 7, 10, 13, 17, 20, 13a
49.	12 B	35.5	850	525	251	11.5	460	12000	100	4800	79	2.60	1.9	23.1	1.32	45.97	27.6	1.4	4.6	3.9	3.15	2, 5, 7, 10, 13, 17, 20, 26, 27, 13b
50.	13 B	44	390	91	5	1	35.5	12000	174	3200	186	1.23				49.9	34.4	2.9	5.9	2.4	0.41	2, 4, 7, 10, 13, 17, 20, 24, 25, 13b
51.	14 B	38	115	52.5	59	3	110	720	209	7100	100	2.40			1.01	47.15	25.0	3.4	9.9	5.8	1.86	2, 5, 7, 10, 13, 17, 21, 24, 25, 27, 13b
52.	15 B	87	282	239	229	3	85	12000	15	6200	151	1.50	4.9	6.4	1.69	45.44	24.9	1.6	8.2	6.4	1.79	2, 5, 6, 10, 13, 17, 20, 24, 28, 13b

No.	Sample number	B	V	Cu	Ni	Co	Cr	Ba	Sr	Ti	Zr	C_{org}	Th	U	K	O	Si	Na	Al	Fe	Mg	Group number
53.	16 B	98	1510	8.3	5	1	162	12000	35.5	2390	65	6.06	0.3	20.4	0.72	47.50	35.17	0.23	3.70	1.07	0	3, 4, 6, 10, 13, 17, 20, 32, 13b
54.	17 A	50	145	330	35	10.4	115	12000	257	57 50	78		13.0	3.0								2, 4, 6, 9, 15, 18, 20, 24, 25
55.	18 A	41	760	37	30.1	3	135	12000	98	5400	112		9.2	8.7	2.96	45.09	27.5	2.4	6.9	1.6	0.85	1, 4, 6, 9, 15, 18, 20
56.	19 A	71	480	19.5	12	3	295	12000	123	6200	148	5.02	11.1	9.9	3.10	47.31	31.8	0.8	6.3	1.0	0.79	3, 4, 6, 9, 15, 18, 20
57.	20 A	57.5	155	25.1	135	3	102	115	182	6800	107	0.05	6.9	1.3								1, 4, 6, 9, 15, 18, 21
58.	21 A	65	50	7.4	13.5	3	41	350	110	2820	52.5	0.29	8.0	2.5	2.55	46.9	33.5	2.9	6.5	1.7	0.52	1, 5, 6, 9, 15, 18, 20, 32
59.	22 A	72	112	12.3	18.2	3	66	1100	71	4000	86	0.08	6.2	4.2	1.79	49.06	31.2	2.2	8.0	2.1	0.42	1, 4, 6, 9, 16, 18, 20, 32
60.	23 A	410	83	18.2	19.1	3	55	500	46	4900	162	5.58	6.1	2.5	2.97	51.53	31.7	0.5	7.2	2.4	0.52	4, 3, 6, 9, 16, 17, 20, 25
61.	24 A	56	95	35	26.3	3	56	910	65	5600	166	0.38	7.6	3.1	1.88	47.76	25.8	2.6	10.3	4.0	1.53	1, 5, 7, 9, 15, 18, 21, 32
62.	25 A	36	102	104	26.9	3	69	930	269	5750	89	0.51	7.6	2.3	1.92	47.78	28.5	2.6	8.9	5.4	1.37	2, 5, 7, 9, 14, 17, 20
63.	A	54	15	5.4	5	3	5	12000	32	1860	110	0.18	10.1	2.6	2.46	47.67	31.2	0.9	8.5	2.1	1.21	1, 5, 7, 9, 14, 17, 20, 26
64.	27 A	43	89	10	5	1	37	590	174	6300	269		1.8	2.2	0.25	47.62	36.2	3.3	5.0	0.04	0	2, 5, 6, 9, 14, 17, 20, 26
65.	28 A	3	740	460	575	18.6	525	630	104	4900	123	1.37	1.1	15.7	0.02	38.86	18.10	0.82	5.32	13.18	5.48	2, 5, 7, 9, 13, 17, 21, 27, 13a
66.	29 C	50	590	178	850	3	83	320	15	410	120	3.80	0.3	41.6								2, 5, 7, 11, 13, 17, 20, 27, 13b
67.	30 B	56	955	159	71	3	85	550	36	2690	170	4.68										3, 5, 7, 10, 13, 17, 20, 25, 13b
68.	31 A	40	79	28.2	17.4	3	52.5	980	330	6500	148	0.42	9.0	2.7	2.37	45.15	26.9	4.0	9.3	4.5	1.02	1, 5, 7, 9, 14, 17, 21
69.	32 C	81	1100	234	480	3	112	12000	15	790	98	3.56				33.76	27.19	0.06	1.74	10.85	0.30	3, 4, 6, 11, 13, 17, 20, 27, 32, 13b
70.	33 C	59	263	95.5	650	11.7	54	91	15	288	126	6.21	0.3	40.5								3, 4, 6, 11, 13, 17, 20, 27, 32, 13b
71.	34 B	91	955	110	340	3	72	12000	15	890	71	4.38				41.39	31.89	0	1.21	7.75	0.17	3, 5, 6, 10, 13, 17, 20, 13b
72.	35 A	3	151	170	56	20.9	350	85	214	6500	35	6.41	0.9	0.2	0.12	46.20	22.60	2.2	10.4	6.6	4.13	3, 5, 7, 9, 13, 17, 21, 13a
73.	36 A	59	132	41	35.5	3	112	830	191	6000	155	5.60	8.1	2.9	2.43	47.1	26.5	2.4	9.4	4.5	1.65	3, 5, 7, 9, 13, 17, 21, 25, 26, 13a
74.	37 A	56	107	38	38	3	83	460	182	4400	93	0.18				48.90	29.74	2.03	7.47	4.50	1.43	1, 5, 6, 9, 13, 17, 20, 25, 13a
75.	38 A	110	155	107	52.5	13.2	126	12000	68	4700	112	0.38	7.2	2.5	3.84	44.45	22.3	0.9	10.9	7.2	2.66	1, 5, 6, 9, 12, 19, 21, 28, 32
76.	39 A	62	162	62	26.9	3	115	12000	390	4800	126	0.18	7.8	6.4	2.94	47.24	24.3	2.3	10.4	6.2	2.3	1, 4, 6, 9, 12, 19, 21, 25, 26
77.	40 B	10	460	53	295	16	74	178	5	760	100	4.13	0.3	19.8	0.43	39.33	29.7	0.6	1.2	12.5	0.09	3, 5, 6, 10, 13, 17, 20, 13b
78.	41 A	126	590	16	41	3	87	200	30	2690	139	2.84	2.1	14.0	1.13	47.28	34.45	0.45	4.06	3.36	0.33	2, 5, 6, 9, 13, 17, 20, 27, 13a
79.	42 B	10	655	93	309	12	47	1740	25	910	126	0.34	0.3	25.7	0.40	37.84	29.3	1.3	1.7	10.8	0	1, 4, 6, 10, 13, 17, 20, 13b
80.	43 C	0	300	176	790	24.5	36	275	20	288	191		1.2	16.5								1, 5, 6, 11, 13, 17, 20, 13b
81.	44 A	110	142	79	49	24.5	79	470	129	5000	91	0.40	6.0	2.4	2.09	46.38	25.82	0.49	6.99	4.92	2.42	1, 5, 6, 9, 13, 17, 21, 28, 32, 13a
82.	45 A	0	204	130	66	36.5	138	435	219	4435	36	0.11	0.3	1.3	0.46	42.51	18.50	1.62	8.04	6.67	5.85	1, 5, 6, 9, 13, 17, 21, 28, 13a
83.	46 A	10	780	115	320	11	112	2040	43	1530	115	4.28	0.3	63.5	0.50	37.34	29.48	0.55	1.92	8.94	0.86	3, 5, 6, 9, 13, 17, 20, 13a
84.	47 C	0	380	186	850	29	85	530	19	620	157	0.68	0.3	37.3	0.20	25.32	14.7	0.9	0.9	25.0	0.59	2, 5, 6, 11, 13, 17, 21, 28, 13b
85.	48 B	0	1000	257	810	40	160	2880	23.5	1260	100	11.50	6.3	42.2	0.71	24.8	16.2	0.9	1.8	22.1	0.55	3, 4, 6, 10, 13, 17, 21, 13b
86.	49 A	0	159	103	162	17	83	80	146	3650	52	0.96	0.6	6.4	0.01	41.95	10.37	0.44	3.47	5.94	6.25	2, 5, 6, 9, 13, 17, 21, 24, 28, 13a
87.	50 A	0	155	49	48	26	49	930	251	5750	69	0	0.6	0.9	0.43	46.46	15.10	1.72	7.87	6.83	3.0	1, 5, 7, 9, 13, 17, 21, 24, 28, 13a
88.	51 A	10	210	22	30	10	59	5100	117	3500	91	1.29	2.9	7.3	1.05	45.92	29.15	1.65	7.73	4.73	2.03	2, 5, 7, 9, 13, 17, 20, 24, 27, 13a
89.	52 B	44	191	166	186	25	120	485	79	4000	72	1.26	0.7	3.5	2.02	36.34	15.7	1.9	7.5	11.2	2.35	2, 4, 7, 10, 13, 17, 21, 24, 27, 28, 13b
90.	53 B	30	990	60	302	14.5	76	2750	17.5	1160	110	4.22	0.3	38.2	0.76	43.77	33.6	1.4	1.8	6.6	0.2	3, 4, 7, 10, 13, 17, 20, 27, 13b
91.	54 A	35	1040	46	182	10	71	2690	35	1480	116	8.23	0.3	40.5	0.81	43.51	33.28	0.26	3.69	4.13	0.38	3, 4, 7, 9, 13, 17, 20, 27, 13a
92.	55 C	0	630	415	760	27	103	380	39	450	151		0.6	47.6	0.74	27.35	15.7	0.6	1.0	23.1	0	1, 5, 7, 11, 13, 17, 21, 26, 27, 13b
93.	56 A	10	1020	24.5	110.	10	72	3500	34	1150	107	5.59	0.3	43.8	0.83	48.48	37.44	0.34	2.05	2.82	0.45	3, 4, 7, 9, 13, 17, 20, 26, 27, 13a
94.	57 A	10	620	66	12	3	102	1740	52	2820	282	8.47	1.2	14.0	1.26	49.48	36.54	1.10	3.47	2.10	0.67	2, 4, 7, 9, 13, 17, 20, 27, 13a
95.	58 A	10	89	10	30	12	54	520	340	3600	129	0.57	4.6	2.2	1.15	46.46	29.29	1.67	8.87	3.96	1.17	2, 5, 7, 9, 13, 17, 20, 27, 13a
96.	59 A	141	126	13	35	14	57.5	690	91	4000	132		6.5	2.4	2.70	48.87	28.06	0.18	7.96	3.95	1.30	2, 5, 6, 9, 13, 17, 20, 25, 13a
97.	60 A	10	350	159	160	14.5	48	195	91	2950	96	1.73	3.0	10.5	1.79	44.31	23.40	0.15	5.01	5.32	1.45	2, 4, 6, 9, 13, 17, 21, 25, 28, 13a
98.	61 A	10	1260	234	380	29.5	95.5	2450	74	2950	141	5.36	1.8	36.3	1.03	44.76	30.90	1.23	3.19	4.62	1.41	3, 4, 7, 9, 13, 17, 20, 26, 27, 13a
99.	62 A	10	720	209	288	19	60	470	49	2690	190	4.90	0.4	24.0	0.91	44.30	28.48	0.17	3.79	8.71	2.00	3, 5, 7, 9, 13, 17, 20, 25, 13a
100.	67 A	126	380	234	410	51	104	288	191	6800	190	0.65	3.5	8.9								2, 5, 6, 9, 13, 17, 21, 28, 13a
101.	68 A	330	350	36	60	12	49	500	214	340	117	2.30	7.4	8.8								2, 5, 6, 9, 13, 17, 21, 24, 28, 13a
102.	69 A	10	107	30	33	17	65	550	148	3950	74	0.26	7.2	1.9	1.75	48.69	29.4	2.5	8.6	4.9	1.85	2, 5, 7, 9, 13, 17, 20, 26, 28, 13a
103.	70 B	141	669	15.5	38	3	85	176	30	3000	138	2.28				51.34	38.3	0.7	3.5	3.6	0.13	2, 5, 7, 10, 13, 17, 20, 26, 13b
104.	71 C	141	151	25.5	33	15	56	1380	105	4000	76	4.38										3, 5, 6, 11, 13, 17, 20, 24, 27, 13b
105.	82 B	35.5	120	43	31.6	9.5	51.	575	102	5100	71	0.22	5.8	3.1								2, 5, 6, 10, 13, 17, 20, 28, 13b
106.	83 B	37	430	263	132	12.9	89	1170	62	4600	34		6.0	11.7								1, 5, 7, 10, 13, 17, 20, 27, 28, 13b

No.	Sample n	Fe	Mg	Group number
107.	84 B			1, 5, 6, 10, 13, 17, 20, 28, 13b
108.	85 A			1, 5, 6, 10, 13, 17, 20, 27, 13b
109.	86 A			2, 5, 6, 9, 13, 17, 20, 27, 13a
110.	87 A			2, 5, 6, 9, 13, 17, 20, 25, 28, 13a
111.	88 A			2, 5, 6, 9, 13, 17, 20, 27, 13a
112.	89 C			1, 5, 6, 11, 13, 17, 20, 28, 13b
113.	90 A			2, 5, 6, 9, 15, 18, 21, 27
114.	91 A			2, 4, 6, 9, 15, 18, 21, 28
115.	92 A			2, 5, 6, 9, 15, 18, 20, 27, 28
116.	93 A			2, 5, 6, 9, 15, 18, 20, 26, 27
117.	94 A			2, 5, 6, 9, 15, 18, 21, 28
118.	95 A			2, 5, 7, 9, 15, 18, 21, 26
119.	96 A			2, 5, 7, 9, 15, 18, 20, 28
120.	97 A			2, 4, 6, 9, 13, 17, 20, 27, 13a
121.	98 A			3, 5, 6, 9, 13, 17, 20, 13a
122.	99 A			2, 5, 7, 9, 13, 17, 20, 26, 27, 13a
123.	100 A			2, 5, 7, 9, 13, 17, 21, 27, 28, 13a
124.	101 A			2, 4, 7, 9, 13, 17, 20, 27, 13a
125.	102 A			2, 5, 6, 9, 13, 17, 21, 26, 13a
126.	103 A			2, 5, 6, 9, 14, 17, 21, 27
127.	104 A			2, 5, 6, 9, 14, 17, 21
128.	105 A			1, 5, 7, 9, 15, 18, 21, 27
129.	106 A			2, 5, 6, 9, 14, 17, 21, 25, 26, 27
130.	107 A			1, 5, 6, 9, 15, 18, 21
131.	108 A			3, 5, 6, 9, 13, 17, 21, 13a
132.	109 A			2, 5, 5, 9, 15, 18, 21
133.	110 A			2, 5, 6, 9, 15, 18, 21
134.	111 A			1, 5, 6, 9, 14, 17, 21, 26
135.	112 A			1, 5, 6, 9, 14, 17, 21, 26
136.	113 A			1, 4, 6, 9, 15, 18, 20
137.	114 B			1, 5, 6, 10, 15, 18, 20, 26
138.	115 B			1, 5, 6, 10, 13, 17, 21, 24, 25, 28, 13b
139.	116 B			1, 5, 6, 10, 13, 17, 20, 24, 25, 28, 13b
140.	117 A			1, 5, 6, 9, 13, 17, 20, 24, 26, 28, 13a
141.	118 A			1, 5, 6, 9, 13, 17, 20, 24, 13a
142.	119 A			1, 5, 6, 9, 13, 17, 20, 26, 13a
143.	120 A			1, 5, 7, 9, 14, 17, 21
144.	121 A			1, 5, 6, 9, 15, 18, 21, 28
145.	122 A			2, 5, 6, 9, 15, 18, 21, 24, 25
146.	123 A			1, 5, 7, 9, 14, 17, 20, 26
147.	124 B			3, 5, 7, 10, 13, 17, 20, 32, 13b
148.	125 A			1, 5, 7, 9, 16, 19, 20, 24, 25
149.	126 A			1, 5, 7, 9, 15, 18, 20
150.	127 A			2, 5, 7, 9, 14, 17, 20
151.	128 A			1, 5, 7, 9, 15, 18, 20, 24, 25, 26
152.	129 A			1, 5, 7, 9, 15, 18, 21
153.	130 A			1, 5, 7, 9, 12, 17, 20, 26
154.	131 A			1, 5, 6, 9, 16, 19, 21, 26
155.	132 A			1, 5, 7, 9, 16, 19, 21, 26
156.	133 A			2, 5, 7, 9, 12, 17, 20, 26
157.	134 A			1, 5, 7, 9, 15, 18, 20, 24, 26
158.	135 A			2, 4, 5, 7, 9, 12, 17, 21, 26
159.	136 A			1, 5, 6, 9, 15, 16, 21, 26
160.	137 B			1, 5, 7, 10, 13, 17, 20, 26, 13b
161.	138 A			1, 5, 7, 9, 12, 17, 21