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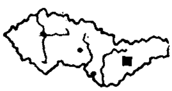
CARBONACEOUS MATTER IN SOME METAMORPHIC ROCKS OF THE NÍZKE TATRY MTS. (WEST CARPATHIANS)

(8 Figs., 10 Pls., 3 Tabs.)



A b s t r a c t: The results of petrological study of metasedimentary schists, and detailed survey of associated carbonaceous matter (CM) are presented. Metasedimentary schists crop out in the migmatite zone on the southern slopes of the Nízke Tatry Mts., in the area of W-Au and Sb-prospection. CM has been studied by a complex of methods (elemental analysis, X-ray diffraction, TEM, SEM, TG and DT analyses, isotopic analysis, analysis of organic matter and gas chromatography). Graphitic (G), semigraphitic (SG) and meta-anthracitic (MA) types, all derived from organic source were distinguished. Coalified phytoclasts are present occassionally in studied samples. The said types of CM indicate different degrees of metamorphism of the host rocks. Bituminous and humic substances in trace amounts in metasediments as well as in mineralized zones are described.

Р е з ю м е: В статье рассматриваются результаты петрографического изучения метаосадочных сланцев и детальное изучение ассоциирующего углистого вещества (УВ). Метасланцы, находятся в мигматитовой зоне в области W-Au и Sb-проспекции на южных склонах Низких Татр. УВ изучалось посредством комплекса методов (елементарный анализ, рентгенографическое исследование, TEM, SEM, TG и DT анализ, изотопный анализ, анализ органического вещества и газовая хроматография).
Были установлены графитовые, семиграфитовые и метаантрацитовые формы УВ, органического происхождения. Кроме того, в некоторых образцах были определены карбонифицированные фитокласты. Данные типы УВ указывают на разные степени изменения материнских пород. В статье также представлены результаты изучения битуминовых и гуминовых субстанций, экстрагированных из метаседиментов и минерализированных зон.

Introduction

The first notices about graphite or graphitic schists from the Sb-mine at Medzibrod (Nízke Tatry Mts.) have been written by K l e i n (1942) and M u n d a (1944). Later on A n d r u s o v—K o u t e k—Z o u b e k (1951) in their trea-

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tise on mineralizations of the Nízke Tatry Mts. mentioned occurence of graphitic schists at the same locality. A brief reference to graphitic matter in certain lithotypes from the area W of Jasenie has been presented by Lukáčik et al. (1977). The results of a more detailed survey of the carbonaceous matter (CM) in the surroundings of Kyslá have been published by Molák et al. (1986).

CM occurs in the area studied (Fig. 1), in disseminated or tectonically concentrated form in metasedimentary schists of various grades of metamorphism, ranging from chlorite zone of the green schist facies (low-grade metasediments) up to the lower stages of amphibolite facies (medium-grade metasediments), (sensu Turner, 1968).

CM-bearing schists are located in the zone of ophthalmitic and stromatitic migmatites and gneisses, belonging to the mantle of the Nízke Tatry Pluton. K/Ar age determinations made on ophthalmitic migmatites and granitoids by Kantor, 1961; Kantor in Molák et al., 1986 gave ages 260—325 mil. y. which date the latest thermic event.

Amount of CM varies considerably, representing generally few tenths of weight per cent, (sometimes less than 0.1 %) but may go up to 1 per cent. Studied rocks were encountered not only by superficial geological mapping, but also in material from boreholes and prospection-galleries driven recently in search for W-Au and Sb-ores. Some of them were detected by geophysical survey (induced polarization) because of their content of graphite and disseminated sulphides (Vybíral, 1986, Michálek et al., 1988).

Several samples of low-grade metasedimentary schists referred to in this paper provided identifiable microfossils of Upper Silurian-Devonian age (Planderová in Molák—Gorek, 1983; in Pulec—Klinec, 1985; Molák et al., 1986; Planderová, 1986).

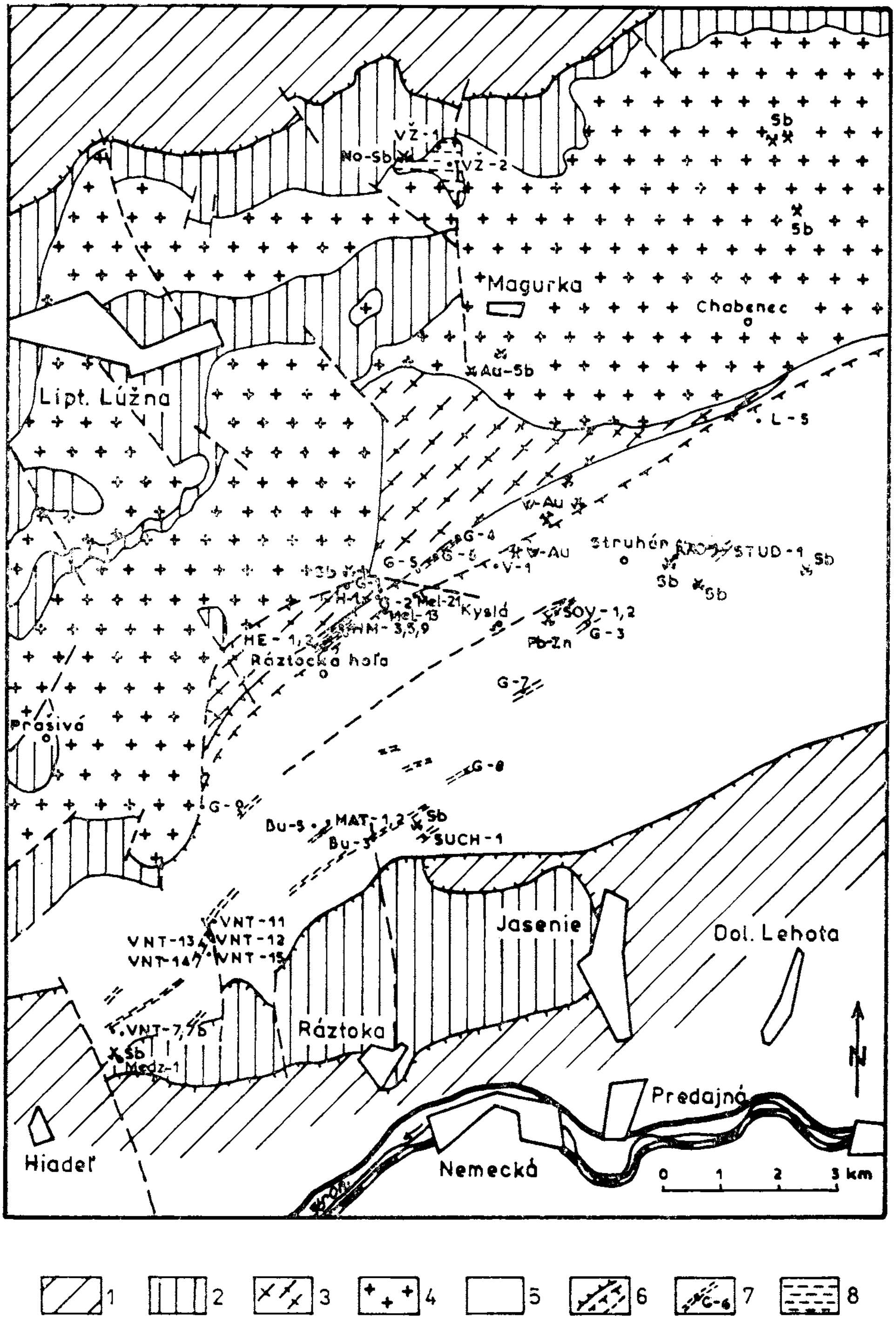
Primary sedimetary features as well as mineral composition of metasediments are often altered by superimposed, retrograde, hydrothermal-metasomatic and cataclastic processes, hampering their identification or discrimination from mylonites and diaphthorites of migmatite. This is why the actual opinion postulating the allochthonous nature of microfossils in studied rocks can not be totally discarded.

Medium-grade metasediments on the other hand acquired in retrograde events the outlook of phyllonites.

Fig. 1. Schematic geological map of central-western part of the Nízke Tatry Mts. (after A. Biely, O. Miko, I. Lehotský, E. Lukáčik, A. Klinec, B. Molák J. Gorek, J. Michálek et al.) with sample locations.

Legend: 1 — Mesozoic nappes; 2 — Mesozoic cover; 3 — nebulitis migmatites; 4 — granitoids; 5 — crystalline schists; 6 — tectonic zones; 7 — strips of metasedimentary schists containing CM with the sample (borehole) number; 8 — biotitic schists "Klinisko".

Crossed hammers — adits or shafts operating, or out of work, with the main metals extracted. Numbers of samples correspond to those refferred to in the text, tables, figures and plates. (Sample Bys-2 taken at the confluence of Bystrianka and Štiavnička creeks in the Bystrá village sample Pol-1 taken at the confluence of Pravá and Ľavá Ráztoka creeks about 3 km N of Polomka village, off the area depicted on Fig. 1.).


Sb
VŽ-1
No-Sb
VŽ-2
Sb
Magurka
Chabenec
Au-Sb
Lipt. Lúžna
L-5
W-Au
G-4
G-5
G-6
W-Au
Struhár
STUD-1
Sb
V-1
Sb
Sb
G-1
H-1
G-2
Mel-21
Kyslá
Mel-13
HM-3,5,9
SOV-1,2
HE-1,2
G-3
Pb-Zn
Ráztocká hoľa
G-7
Prašivá
G-8
G-9
Bu-5
MAT-1,2
Sb
Bu-3
SUCH-1
VNT-11
VNT-12
VNT-13
VNT-14
VNT-15
Jasenie
Dol. Lehota
VNT-7,7b
Sb
Medz-1
Ráztoka
N
Predajná
Hiadeľ
Nemecká
0 1 2 3 km
1
2
3
4
5
6
G-6
7
8

Tectonic setting of metasedimentary schists in migmatitic and gneissic environment is diverse: those, containing poorly crystallized CM and/or microfossils are in discordant tectonic position, whilst those, bearing graphitized CM are located conformably. The thickness of metasedimentary intercalations varies from a couple of metres up to few decametres.

Our endeavour to unveil the origin, petrological and metamorphic character of the studied rocks and associated CM is justified also by the fact, that they are located within the ore-bearing zone.

Petrological observations

Metasedimentary schists only scarcely display relic sedimentary textures. Characteristic associations of metamorphic minerals are as follows:

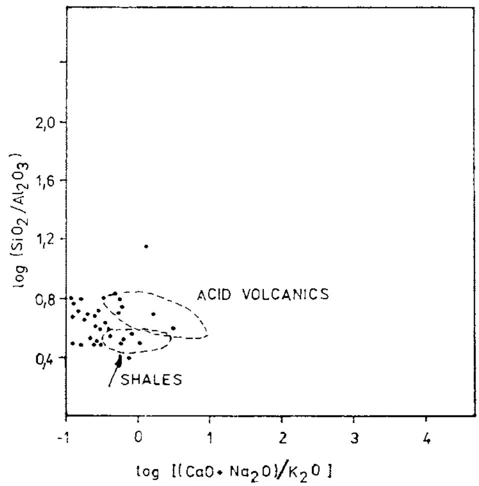
quartz + muscovite + rutile ± chlorite + metaanthracite ± semigraphite;
quartz + muscovite + chlorite + biotite ± rutile + semigraphite;
quartz + plagioclase + muscovite + chlorite + biotite + sphene ± semigraphite + graphite;
quartz + plagioclase + biotite ± graphite.

Secondary alterations generally present are sericitization, carbonatization, formation of radial aggregates of tourmaline, euhedral apatites and muscovites often having symplectic texture. Comparing the chemical composition of migmatites and metasediments we can observe that the later are generally lower in SiO_2, CaO and Na_2O while they are relatively richer in Al_2O_3, Fe_2O_3, FeO, MgO, TiO_2, P_2O_5, MnO, K_2O and S (chemical analyses from the report of P e c h o et al., 1984 have been used). Their original composition must have been different from that of migmatites, nevertheless an influence of superimposed alterations should also be taken into account. Both lithologies differ considerably also in contents of trace elements. Metasedimentary schists possess higher average values of W, Sb, Ti, B, La, As, Be, Th, Rb, Hf, Cs, V and in turn they contain very little Nb and Ta. Mean Th/U ratio is 3, 1. The transitional zone between metasediments and ophthalmitic migmatites is locally formed by biotitic and garnetiferous gneisses. The zone of nebulitic migmatites is characterized by the association: quartz + plagioclase + K-feldspar + biotite + muscovite ± sillimanite + garnet ± graphite, whilst the zone of stromatitic and ophthalmitic migmatites and gneisses by the association: quartz + K-feldspar + + plagioclase + biotite + muscovite + garnet.

Neither staurolite-chloritoid, staurolite-andalusite nor staurolite-sillimanite, zone was identified by our survey in the area of the Nízke Tatry crystalline rock complex.

In order to determine the protolith of metasediments 27 chemical analyses of superficial as well as borehole samples were used for the correlation of main oxides. Owing to above mentioned secondary alterations the reliability of determined protolith is more or less reduced. Obtained values were plotted in the diagrams of G a r r e l s—M a c k e n z i e (1971), E w a r t (1979) and De La R o c h e (1966), (Figs. 2, 3 and 4). (Chemical analyses were performed at the Geological Institute of D. Štúr Bratislava and at the Geological Survey Spišská Nová Ves).

Fig. 2. Diagram of logarithmic relationships of oxides; the field of Cenozoic volcanic rocks after Ewart (1979), field of shales after Garrels — Mackenzie (1971). Figurative points of the chemical analyses of low-and medium grade metasedimentary schists from the Nízke Tatry Mts. crystalline complex. Samples: G-1, G-2, G-3, G-4, G-5, G-7, G-8, G-9, HM-3, HM-4, HM-5, HM-6, HM-7, HM-8, HM-9, HE-2, Bu-3, L-5 (122.9 m), V-1 (405.3 m; 419.5 m; 492 m 499.7 m) VNT-12 (38.5 m; 187 m), VNT-15 (144 m; 235 m).



Original sediments consited mainly of shales and arcoses, with minor rhyolitic and locally also basic volcanoclastic admixture. Surrounding migmatites in turn were, according to the survey of Hovorka (1975), derived from greywackes. Primary flyschoid eugeosynclinal sediments contained intercalations of quartz-arenites, argillaceous and calcareous shales and rocks with bituminous admixture (Hovorka l. c.).

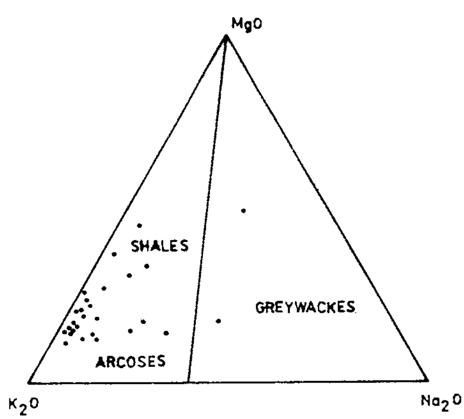


Fig. 3. Diagram of K_2O—MgO—Na_2O values after De La Roche (1966) Figurative points of the same set of samples as in Fig. 2.

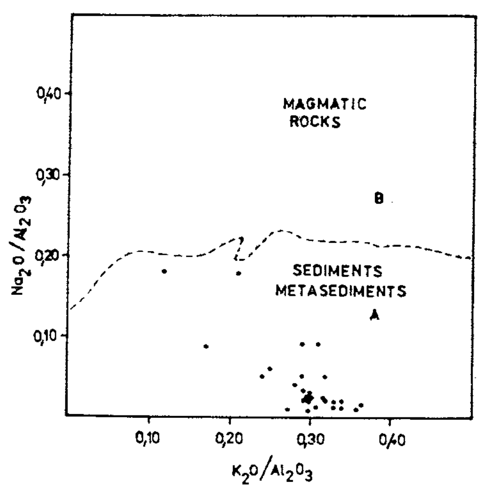


Fig. 4. Diagramatic plot of Na_2O/Al_2O_3 vs K_2O/Al_2O_3 values after Garrels — Mackenzie (1971) with fields of sedimentary and metasedimentary rocks (A) and magmatic rocks (B). Figurative points of the same set of samples as in Fig. 2.

Protoliths of amphibolites, amphibolitic gneisses and paragneisses, intercalated in migmatites at Kyslá N of Jasenie were considered recently by P i t o ň á k—S p i š i a k (1988). They found out that amphibolites contained up to 25 % of terrigenous sedimentary admixture while typical paragneisses up to 25 % of basic volcanic material.

The whole suite of genuine sediments was probably deposited in the littoral portion of a Devonian basin, supplied by clastic material from the mainland cordilleras and from continental as well as submarine volcanic centres. Relatively calm periods with deposition of shales and arcoses alternated with the periods of tectonic activity, accompanied by the sedimentation of poorly sorted material.

Quantitative analyses of REE made on 21 samples of metasedimentary schists revealed higher amount of LREE, especially La. Analyses where normalised by average European, North American and Russian shales, after P i p e r (1974). (Fig. 5).

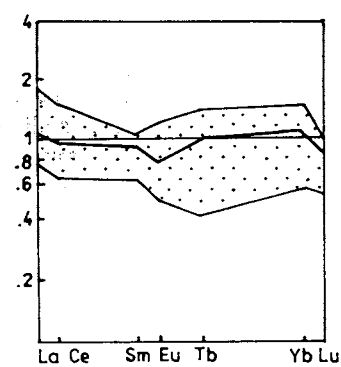


Fig. 5. Fields of distribution of REE in metasedimentary schists in the area studied and in granitoids of the Nízke Tatry Pluton. (Normalized by shales, P i p e r, 1974).

Dotted field delimitates the minimum and maximum values whilst bold line represents the average value of whole set of samples. Average contents of REE in migmatites, granitoids, amphibolites and their tectono-metamorphic derivates, presented in report of G b e l s k ý et al. (1985) falls distinctly below the line of studied samples. It is worth to mention, that the most prominent ore mineral-scheelite is also enriched in LREE (H v o ž ď a r a, 1985). Higher values of LREE, especially La indicate crustal origin of the primary material in metasediments. Negative Eu anomaly indicates possible removal of plagioclase from the source rocks.

Table 1

REE contents (in ppm)

Sample	La	Ce	Sm	Eu	Tb	Yb	Lu
G-1	56.0	82.6	6.16	1.62	1.09	4.26	0.43
G-2	31.3	56.0	5.09	0.90	< 1	4.51	0.49
G-3	40.5	86.4	6.02	1.74	< 1	3.73	0.56
G-4	54.0	89.7	6.92	1.49	< 1	2.00	0.33
G-5	38.9	62.9	7.03	1.22	1.19	4.12	0.63
G-7	43.1	75.5	5.65	0.80	1.51	3.20	0.55
G-9	67.6	112.0	6.74	1.23	1.52	3.22	0.49
HM-3	52.6	95.7	7.10	0.80	1.46	4.41	0.55
HM-5	50.5	80.8	6.99	1.38	1.31	3.53	0.45
HM-7	43.4	70.9	7.16	1.07	1.56	3.62	0.50
HM-8	36.2	69.3	5.05	1.00	1.13	3.74	0.37
HM-9	26.3	43.3	4.87	1.04	1.64	11.5	1.70
HE-2	48.5	75.3	6.70	0.78	1.16	3.79	0.43
HE-3a	48.5	82.9	7.59	1.02	1.40	3.53	0.57
L-4	33.1	62.8	4.78	0.95	1.11	3.06	0.32
L-5 (107 m)	36.9	65.4	5.95	0.99	1.39	3.84	0.50
L-5 (123 m)	51.4	83.5	7.13	1.23	1.47	4.28	0.73
V-1 (405.3 m)	47.3	84.9	6.95	1.46	1.43	2.89	0.45
V-1 (419.5 m)	55.0	91.8	7.12	1.47	1.43	3.73	0.32
V-1 (492.0 m)	41.7	73.0	6.19	0.94	1.03	2.98	0.51
V-1 (499.7 m)	44.1	82.2	7.12	1.74	1.50	4.59	0.63

(The evaluation of REE was carried out by INAA at the Laboratory of Geoindustria, Praha, V. Moučka).

Methods

Prior to application of analytical methods the extraction of CM was made by flotation of the powdered samples at the interface of toluene and water (1 : 5) and by treatment of the floating residue with hot, concentrated hydrochloric and hydrofluoric acid. Removal of synthetic phase and very fine-grained pyrite was effected by addition of powdered zinc and dilution in HCl. Consistent multiple rinsing of the preparate with hot distilled water was made between each step of extraction.

Elemental analysis

Extracted CM was submitted to the elemental analysis. Contents of C, H and N were measured in a Carlo Erba analyser, model 1104 at the Chemical Institute of the Comenius University in Bratislava.

The analytical conditions were as follows:
0.8—1.0 mg of the sample was combusted at the temperature of approx. 1000 °C in a helium (oxygen) flow. Combustion catalyzators Cr_2O_3, CoO, Co_2O_3 + Ag, reduction agent: Cu. The analyser was calibrated by means of a standard between each measurement. Few samples were tested also sulphur content.

Table 2

The results of elemental analysis, sulphur determination and H/C atomic ratios

Samples	elements (in wt %)				
	C	H	N	S	H/C
1. VNT-7 (81.5 m)	70.70	0.03	—	—	0.005
2. VNT-11 (92 m)	86.19	0.08	—	2.07	0.01
3. VNT-13 (27 m)	94.38	0.05	—	0.67	0.006
4. MAT-1	97.16	0.11	—	—	0.01
5. MAT-2	95.97	0.04	—	2.7	0.005
6. MEDZ-1	92.66	0.03	—	0.96	0.004
7. G-1	89.11	0.97	—	—	0.13
8. G-3	59.37	0.85	—	—	0.17
9. G-8	41.63	2.15	—	—	—
10. HE-2	26.80	0.90	0.63	—	—
11. HM-5	31.68	0.17	0.47	—	—
12. L-5 (107 m)	57.91	0.65	—	—	0.14
13. MEL-13	13.33	—	—	17.16	—
14. MEL-21	83.19	0.28	0.14	—	0.04
15. SOV-1	87.33	0.20	0.26	—	0.03
16. BYS-2	80.67	0.34	—	—	0.05

analyst: E. Greiplová

Elemental analysis has shown that several extracts retained high amounts of mineral phase, especially those, present in disseminated form. Two types of CM could be distinguished: the first with very low H/C atomic ratio (0.004—0.01) represented by graphites and the second with somewhat higher H/C ratio (0.03—0.17) pertaining to subgraphitic phases (SG, MA). Owing to high amount of mineral phase in several samples we did not calculate their H/C atomic ratios. Minerals generally present in extracts are rutile, pyrite, tourmaline, apatite zircon and sphene. The first two of them are bound intimately to subgraphitic CM and we failed to separate them from each other.

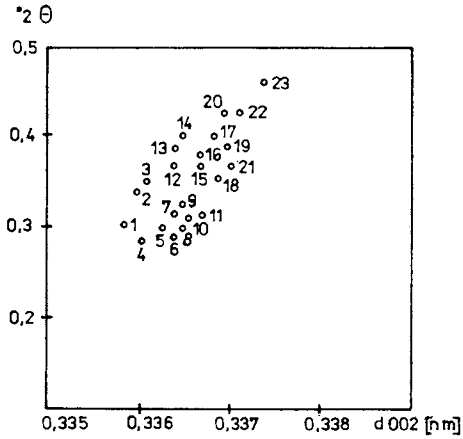
X-ray diffraction analysis

Extracts containing no considerable admixture of mineral or synthetic phase mixed with a standard (silicon, d 002 0.3138) were mounted in a Philips 1050 with a goniometer 1050, operating with crystal reflected Ni-filtered CuKα-radiation and x-rayed in order to measure the lattice parameters of graphitic or subgraphitic substances.

At least 4 measurements were made on each preparate and d 002 values were evaluated. Arithmetic means of the interplanar distances and crystallinity indexes were plotted in a diagram (Fig. 6). Comparing our results with the graphite thermometer of Shengelia et al. (1977) it became obvious that the majority of samples falls within the metamorphic temperatures of 380—480 °C, which points to the green schist facies of metamorphism.

On the other hand some samples (MAT-1, VNT-11 (7 m, 51.5 m) have been exposed to temperatures as high as 650 °C i. e. amphibolite facies.

Fig. 6. Diagram showing the relationship between interplanar distances d 002 and crystallinity indexes, characterized as width of the 002 peak at half of its height. Samples: 1 — MAT-1; 2 — VNT-11 (51.5 m); 3 — VNT-11 (7 m); 4 — G-1; 5 — VNT-12 (38.5 m); 6 — VNT-15 (179 m); 7 — VNT-15 (75.2 m); 8 — VNT-15 (235 m); 9 — VNT-12 (14 m); 10 — VNT-15 (114 m); 11 — VNT-2 (96 m); 12 — L-5 (106.9 m); 13 — VŽ-1; 14 — MAT-2; 15 — VNT-7 (81.5 m); 16 — SOV-2; 17 — Pol-1; 18 — SOV-1; 19 — VNT-15 (235 m); 20 — VNT-13 (22 m); 21 — VNT-7b (133.3 m); 22 — BYS-2; 23 — G-3.



Thermo-gravimetric (TGA) and differential thermal analysis (DTA)

(TGA were perfomed on a Du Pont 1090. Analytical conditions: sample size: 1.15-3.26 mg, heating rate — 20 °C/min., atmosphere-air; analyst: E. Gál, VÚKI, Bratislava. DTA were carried out on a Du Pont 990 instrument. Analytical conditions: Al_2O_3 puffer, heating rate 10 °C/min., static air. Analyst: I. Horváth, ÚACH SAV, Bratislava.

TGA has been applied to measure the weight changes in the CM depending upon the temperature and DTA for measuring the enthalpy changes as a function of temperature.

TGA has shown that maximal rate of weight loss ranged from 627 °C to 678 °C (average 657.5 °C) for low-grade graphites and 730—819 °C (average 764.5 °C) for medium-grade graphites. These values are significantly lower in respect of the comparative sample ČK-MV (taken from the graphite deposit Český Krumlov — Městský Vrch), metamorphosed under conditions of amphibolite facies, which gave 849 °C.

DTA studies on CM extracted from the samples G-2, G-5, G-8, G-9, HE-1, HE-2, showed the range of major exothermic effects between 605 and 660 °C (average 631 °C), indicating low-grade graphites and/or turbostratic carbon. Samples G-3 and Pol-1 gave identical value of 725 °C, while maximal exothermic effect in the sample ČK-MV was recorded at 885 °C.

The variations in the rate of weight loss and/or maxima of exothermic effects reflect essentially the oxidation tendency of the studied materials as a function of their degree of crystallinity. Only insignificant shifting of the above values could have occurred on account of impurities in extracts or other factors.

Either of the two thermic methods exhibited two types of CM: graphitic showing higher T max values was formed under conditions of amphibolite facies, and subgraphitic (SG, MA) with lower values of T max, formed under conditions of biotite or (chlorite?) zone of the green schist facies of metamorphism.

Transmission electron microscopy (TEM)

This method has been applied especially to extracts retaining high proportion of mineral phase even after repetition of acid treatment, or in those cases, when the volume of CM obtained was too low for study by conventional methods.

Samples for TEM were prepared either by direct transfer of tiny particles of finely ground CM on the Formwar coated single slot copper grid, or by spreading of the preparate on the surface of distilled water and picking up the floating particles on the Formwar filmed copper grid as described by Bonijoly et al. (1982).

Particles of CM thin enough for transmitting electrons were subjected to selective area diffraction (SAD). Those possessing no threedimensional crystalline structure yielded reduced number of diffraction rings or even diffuse SAD patterns (e. g. plates VI/6, IX/3, 5). On the other hand true graphites exhibited typical mono-or polycrystalline diffraction patterns, from which orientation of graphite plates or interlayer spacings (d hkl) could be determined. Precise calculation however requires an internal standard as to eliminate random errors esp. on account of the apparature setting.

Dark field technique enabled us to observe the coalescence of basic structural units, which increases with the degree of crystalline perfection. This technique has been demonstrated in detail by Boulmier et al., 1982; Oberlin and Oberlin (1983) and others. Coexistence of transitional phases of CM and vestiges of microorganisms with more or less graphitized forms were detected frequently in some samples. A similar observation was stated e. g. by Mc Cartney—Ergun (1965), Kwiecińska (1980), Landis (1971) and others.

Some of the poorly crystallized particles are marked by elliptic SAD pattern (Plates VII/2, VIII/3) obtained in the reciprocal space image. They are probably composed of fibres and represent primary organic structures of CM which inhibited consistent graphitization of the material. Similar patterns, although obtained on artificial preparates, were described by Oberlin (1979).

Several particles of CM studied by TEM retained relic organic features (e. g. Plates VI/6, VII/1; VIII/2, 4, 5, 6, 7; IX/1, 2, 4; X/6) even though they are no more valuable for biostratigraphical purposes (oral communication by E. Plan_derová). They could have been originally inertinite phytoclasts, such as those described by Bostick (1974), Diessel—Offler (1975), Kwiecińska (1980).

Energy dispersive X-ray spectrometer (EDS), attached to the electron microscope, has been utilized in order firstly to select grains of carbon free of any inclusions (i. e. possessing no characteristic peaks of elements with atomic number higher than 11) and secondly for the study of inclusions themselves and the associated mineral phase.

Following elements have been determined by EDS: Ca, Si, Al, Ti, Mn, Cr, Fe, Au, K and S. In the sample BU-5 possibly a tiny muscovite crystal is trapped in carbonaceous shell since the elemental composition shows low characteristic peaks of Si, Al and K. Muscovite is a common constituent of the host rock, too.

In sample HE-1 peaks of Al, Si, Ca and Mn appeared, which could indicate a garnet inclusion. One analysis ascertained the presence of Cr, Fe (chromite?) and gold in the same sample (Plate X/6). These minerals form particles not exceeding 10 mm in diameter enclosed in CM. (Transmission electron micrographs were obtained from the JEOL JEM-200CX and JEM-100 C).

Scanning electron microscopy (SEM)

Preparates of extracted CM were studied by SEM. A JEOL JSM-840 installed at the D. Štúr's Institute of Geology operated by RNDr. F. Caňo has been utilized. This method enabled us to observe the habit and size of CM particles as well as their deformations. It has been confirmed, that the size of carbonaceous particles generally depends upon metamorphic grade of the host rock. Thus largest graphite flakes have been encountered in the granulite facies (Plate I/1, 2) whereas in various zones of amphibolite facies (Plates I/4, 5; III/1, 2, 6) their size gradually decreases down to lower degrees of green schist facies, characterized by rapid reduction of grain size (Plate IV).

Other factors however, such as type of source material, geological age, and pressure should also have some influence on the grain size of graphitized CM.

Carbon isotope analyses

Genetic aspects of the disseminated (or concentrated) CM collected from metamorphic rocks were studied by stable isotope methods.

About 5 mg of sample (depending on carbon concentration) was combusted to CO_2 in an oxygen-helium flow at 900 °C, cleaned for sulphurous and nitrous gases and water and transferred to glass ampules by freezing with liquid nitrogen. The CO_2-gas was measured for $^{13}C/^{12}C$ composition in a Varian MAT 250 triple collector mass-spectrometer at the Department of Geology, University of Copenhagen.
Analytical results were corrected for mass 46 contributions and recalculated to δ-values*. The results are reported as per mille (‰) deviations from the PDB-standard. Reproducibility measured as standard deviation on 10 standard preparation is better than 0.03 ‰ on the δ-scale.

All investigated samples are depleted in ^{13}C as compared to inorganic carbon found in limestones and hydrothermal carbonates. In general, the observed values correspond to organically derived carbon (Fig. 7). An inorganic origin, e. g. from ^{13}C-rich carbonate rocks or from a deep, well-homogenized source (e. g. carbonatite), is thus very unlikely. In the majority of samples only negligible alteration of the original $^{13}C/^{12}C$-ratios is presumed to have occurred during superimposed stages of metamorphism, as the host rocks did not contain carbonates and isotopic re-equilibrium thus could only have taken place to a limited degree. Moreover, any re-equilibrium would have produced more ^{13}C-enriched CM rather than the very ^{13}C-depleted values observed here.

The metasedimentary schists underwent only low- or medium-stages metamorphism and considerable re-equilibrium with eventual carbonate rocks would not have resulted. Relatively heavier carbon of the samples G-1 and HM-5 may be explained by the fact that they originate from fault zones and/or from zones

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* $\delta = \frac{R(\text{sample}) - R(\text{standard})}{R(\text{standard})} \times 1000\ ‰, \quad R = \frac{^{13}C}{^{12}C}$

of hydrothermal activity, where reactions with hydrothermal fluids could have taken place. Similar effects have been indicated by Andreae (1974) from the Arendal region of Norway.

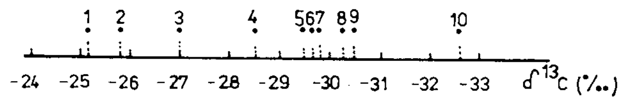

Fig. 7. Isotopic composition of the carbonaceous matter extracted from the metasedimentary schists of the Nízke Tatry Mts. crystalline complex. Samples: 1 — G-1; 2 — HM-5; 3 — VNT-12 (14 m); 4 — VNT-15 — 235 m); 5 — VŽ-1; 6 — VNT-15 (75.5 m); 7 — BYS-2; 8 — VNT-7 (81.5 m); 9 — G-3; 10 — Pol-1.

We thus find no indication that the investigated CM should have any other origin than as primary organic matter. Comparing our results to the data of Schidlowski (1986), the progenitors could have been eukaryotic algae, anaerobic bacteria or chemoautotrophic bacteria. Most of the observed δ-values are compatible with other observations of Lower Palaezoic organic matter (e. g. Buchardt et al., 1986; Schidlowski, 1986). Some of the samples, however, contain very ^{13}C-depleted carbon (e. g. VNT-7, G-3, Pol-1), and may have originated from older sources. According to the carbon isotope age curve presented by Schidlowski (1986), $\delta^{13}C$-values of organic matter as low as -35 ‰ occurred approx. 900—1000 m. y. ago (Upper Proterozoic). Galimov (1980) pointed out that $\delta^{13}C$-values ranging from -28 to -38 ‰ are characteristic for kerogens from the Russian Platform older than 2 b. y.

In summary we may assert that there seems to exist no difference among ^{13}C-values in response to the degree of crystallinity of CM. True graphite (G-1) exhibits similar values as poorly ordered CM. The same is compliant for samples G-3 and Bys-2 (semigraphites) and samples from boreholes VNT-7, 12 and 15 (graphites) respectively. Sample VŽ-1, extracted from the so called "Klinisko" schist is compatible with the rest of samples as far as its carbon isotope composition is concerned.

Analysis of organic matter (OM)

Besides the residual CM, the studied samples also contain small amounts of bitumens and humins. C_{org}/C_{bit} and/or C_{org}/C_{hum} ratios are in the majority of samples very high. Since the retention of primary bitumens and humins in biotite zone or amphibolite facies of metamorphism is very improbable we presume that they are of migrated nature (Tab. 3). Moreover traces of bitumens in mineralized zones, represented by silicified scheelite-bearing migmatites and amphibolites, quartz-hematite breccia from an old-Sb mine Krokľová (sample KRO-1 approx. 800 m E of Struhár), and vein baryte from the dump of Pb-Zn mine, Sovliansko (SOV-2) were detected. On the other hand the proportion of bitumens (17—29 %) and humins (14—63 %) relative to total organic carbon is here very high. Both substances are of migrated nature too.

Table 3

Analysis of organic matter

Sample № borehole (depth)	Total of org. mater (%)	Total of org. corbon (%)	Carbon residual (%)	Carbon bituminous (%)	Carbon humic (%)	Relative content of C residual (%)	Relative content of C bitumin (%)	Relative content of C humic (%)	Content of carbonate $CaCO_3$ (%)
G-3	0.967	0.761	0.750	0.006	0.004	98.5	0.8	0.5	0.0
G-4	0.116	0.091	0.082	0.006	0.003	89.9	6.6	3.3	0.6
G-5	0.080	0.063	0.055	0.005	0.003	87.0	8.1	4.7	0.6
G-7	0.137	0.108	0.101	0.005	0.001	93.6	5.4	0.9	0.0
G-8	0.157	0.123	0.117	0.004	0.001	95.2	3.3	1.3	1.3
G-9	0.207	0.163	0.156	0.006	0.001	95.5	3.8	0.6	1.9
HM-9	0.130	0.102	0.092	0.006	0.002	90.5	6.5	2.9	1.0
BU-3	0.032	0.025	0.015	0.007	0.004	57.0	27.2	15.6	1.6
BU-5	0.038	0.030	0.011	0.006	0.012	39.1	20.2	40.5	1.1
Sov-1	0.240	0.189	0.184	0.003	0.000	97.8	1.9	0.1	13.6
Such-1	0.101	0.080	0.074	0.003	0.002	92.1	4.3	3.4	0.8
VŽ-1	0.133	0.105	0.099	0.003	0.002	93.9	3.4	2.6	1.1
VŽ-2	0.109	0.086	0.079	0.002	0.004	90.7	3.3	5.8	1.2
V-1 (401.6 m)	0.536	0.422	0.414	0.005	0.001	98.3	1.3	0.3	8.7
V-1 (419.5 m)	0.017	0.013	0.003	0.002	0.003	56.0	17.0	26.8	7.8
L-5 (107.5 m)	0.061	0.048	0.046	0.002	0.000	95.2	4.7	0.0	17.3
L-5 (122.9 m)	0.040	0.031	0.026	0.002	0.003	79.5	8.0	12.3	9.1
L-5 (171.5 m)	0.026	0.021	0.016	0.003	0.001	77.1	17.7	5.1	10.6
VNT-7 (81.5 m)	1.233	0.971	0.959	0.011	0.000	98.7	1.2	0.0	12.4
VNT-7b (133.3 m)	0.818	0.644	0.633	0.008	0.002	98.3	1.2	0.4	3.7
VNT-15 (119.0 m)	0.798	0.628	0.622	0.003	0.003	98.8	0.5	0.5	19.4
VNT-15 (176.9 m)	0.089	0.070	0.062	0.003	0.005	86.9	4.9	8.0	1.2
VNT-15 (180.2 m)	0.866	0.682	0.676	0.002	0.003	99.0	0.4	0.4	9.0
Bys-2	0.227	0.179	0.166	0.008	0.003	92.2	4.9	2.0	10.5
STUD-1	0.063	0.049	0.041	0.003	0.006	79.8	7.1	13.0	6.2

Analyses were performed at the Moravian oil Company in Hodonín by drs. Kotásek and Koukolíček et al.

Bitumen extracts from few samples were submitted to gas-chromatographic analyses.

A Carlo Erba GL 452, operating at Chemical Institute of the Comenius University in Bratislava has been used. Analyses were performed by I. Ostrovský CHÚ UK Bratislava, and V. Harča, GÚDŠ Bratislava. Analytical conditions: Fl detector on capillary column with a stationary phase SE-52, temp. 200 °C.

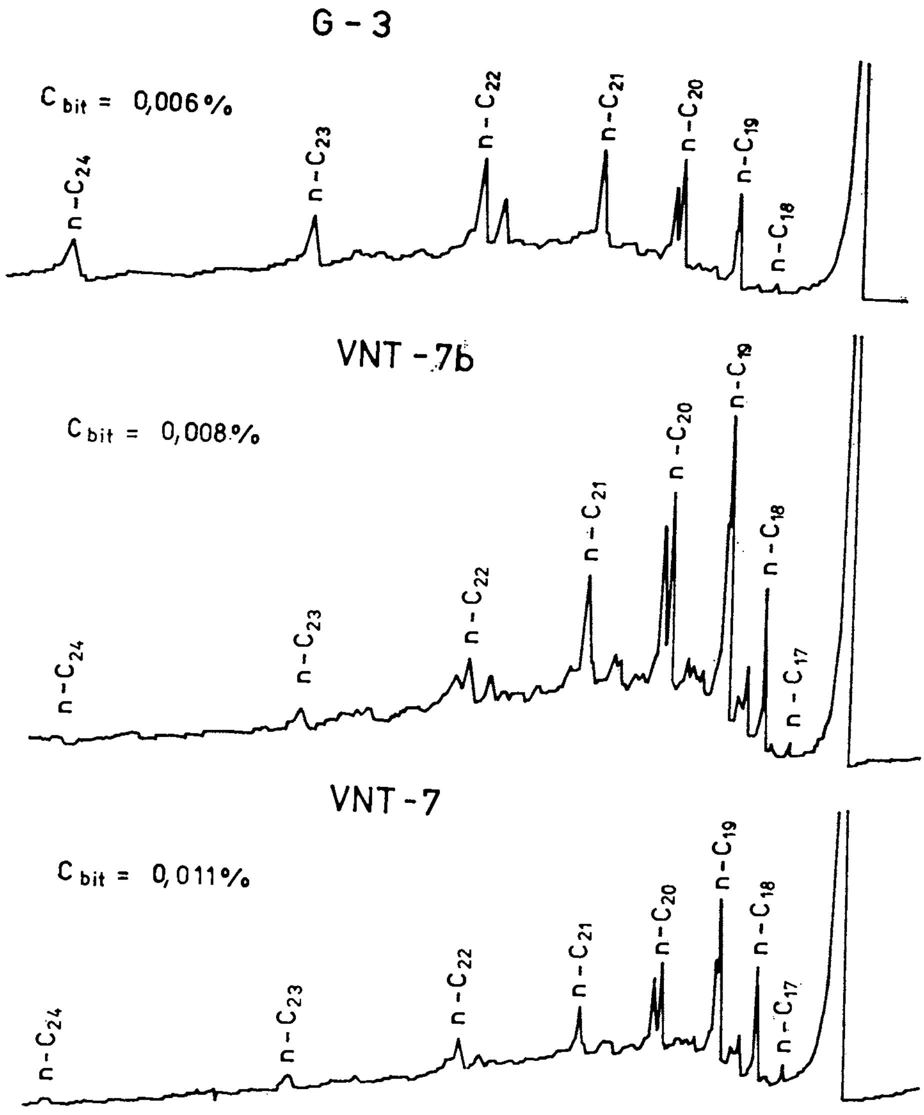

Fig. 8. Gas-chromatograms of bitumen extracts. Samples: VNT-7, VNT-7b — Medzibrod, Sample G-3 — Soviansko—Haliar.

In the chromatograms (Fig. 8) two types of distributions of n-alcanes are distinguishable: the first with maxima at n-C_{19} (samples from boreholes VNT-7 and 7b) and the second with the maximum around n-C_{22} (sample G-3).

The results of analyses indicate that primary organic substance in former samples underwent a stronger temperature alteration than the later. This observations is in good agreement with the degree of metamorphism of residual CM in studied samples, too.

Presence of bitumes has been proved by many authors in deposits of Hg, Pb-Zn, Ag-Co-Ni, Cu, Au, fluorite-baryte etc. as referred by Kříbek (1981). Gaseous, liquid and solid carbonaceous substances also occur in hydrothermal uranium deposits.

There are generally two opinions on the origin of these substances: the first concluding, that bitumens have abiogenic precursor and were formed by synthesis from gases (H_2, CO_2, CH_4), released during degassation of the Upper Mantle.
The second postulates a process of distillation or pyrolysis of OM of the host rocks, affected by heat flow or hydrothermal solutions.

The finding of bitumens and humins in ore-bearing rocks and vein fillings in the area of W-Au, Sb and Pb-Zn-barite mineralizations (amounting up to 0.017 weight percent) provides an evidence of the migration of organic substances in hydrothermal processes. So they could have taken part also in the ore--forming processes.

The source of organic substances remains still unknown. Oxidation of OM during a hydrothermal process might be one of the causes of the lowering of redox potential of hydrothermal solutions, leading thus to accumulation of the ore components as suggested by Kříbek (l. c.).

Conclusions

Metasedimentary schists belonging to various zones or facies of metamorphism crop out in migmatitic complex in the area of W-Au and Sb prospection north and west of Jasenie (Nízke Tatry Mts).

Mineral and chemical composition of metasedimentary schists differs from that of migmatites, and gneisses. They are lower in SiO_2, CaO and Na_2O while they are richer almost in all the rest of common oxides and a number of trace elements (W, Sb, Ti, B, As, Be, Th, Rb, Hf, Cs, V). Average contents of REE show a distinct affinity to average shale-value presented by Piper (1974). Mean contents of REE in migmatites, gneisses, granitoids and amphibolites fall below the line of average metasediments.

The protoliths of metasedimentary schists should have been arcoses and shales with minor acid and/or basic volcanic admixture whilst migmatites originated predominantly from greywackes. Owing to superimposed alterations the reliability of protolith determination is more of less reduced.

Low-grade metasediments, containing subgraphitic CM (SG, MA) and locally also microfossils of Lower Palaezoic age, are located tectonically in migmatitic environment whereas medium-grade metasediments, containing graphitic CM form integral part of migmatite zone and are in general positioned conformably. Regardless of different degrees of metamorphism of metasedimentary schists their formation must have had much in common because of similar chemical composition, distribution of REE and isotopic composition of associated CM.

At least three types of CM are present: G, SG and MA. They are characterized by following parameters: *G type* — very low H/C atomic ratio (less than 0.01), 002 interlayer spacing not exceeding 0.337 nm, high temperatures of maximal weight loss (average 765 °C) and maxima of exothermic effects, SAD patterns with characteristic graphitic reflections, including 101 and 112 lines, relatively coarse grain size. *SG type* — exhibits still low H/C value (up to 0.1), 002 interlayer spacing between 0.337 and 0.338 nm, lower temperatures of max. weight loss (average 658 °C) and exothermic maxima (average 630 °C), smaller grain size and SAD pattern with reduced number of reflexions, 101 and 112 reflections sometimes missing *MA type* — higher H/C values (0.1 or more), d 002 above 0.338 nm, low temperatures of T_{max}, further reduction of SAD reflections and rapid decrease of grain size. Majority of observed phytoclasts in studied samples possess MA-, or turbostratic texture, exhibited by diffuse SAD patterns. Phytoclasts not only testify biogenic of CM but also are an indicator of relatively low conditions of thermic metamorphism (chlorite zone).

G (± SG) phases have been formed under metamorphic conditions of amphibolite facies, whilst MA and SG phases indicate conditions of chlorite or biotite zone of the green schists facies.

Coexistence of the two complexes comprising low — resp. medium-grade graphites can be explained tectonically. In fact numerous subparallel north-east trending fault zones separating both lithologies were distinguished in the area.

Mineralized waters springing locally out of them contain considerable amounts of mineralization (Ca — (Mg) — HCO_3 — Si type) and CO_2 (Dovina — Rapant, 1983). Mineral water from the spring at Kyslá yielded $\delta^{18}O$ value of — 10.78 ‰ (SMOW) whereas water from borehole H-1 (Husárka) gave — 11.67 ‰ (SMOW), thus demonstrating deep circulation of meteoric water (Kantor et al., 1985).

Isotopic research of CM disclosed that it is composed of relatively light carbon and generally does not show considerable scatter of $\delta^{13}C$ values. Slightly lower values exhibit the samples collected from tectonic zones, which is probably due to the effects of hydrothermal fluids. Some of the samples, contain very ^{13}C depleted carbon (e.g. VNT-7, G-3, Pol-1) which may have originated from Precambrian source.

Besides residual carbon metasedimentary schists also contain traces of bituminous and humic substances of migrated nature. Two types of bitumens have been distinguished: the first with maximum distribution of n-alcanes at n-C_{19} and the second with maximum at n-C_{22}. The first seems to have passed higher temperatures of metamorphism compared to the second, which is in a good agreement with the degree of crystallinity of residual carbon in respective samples.

The presence of bitumens in W-, Fe-, Sb- and Ba- mineralized zones in the area provides an evidence of their migration in hydrotermal solutions and possible role in ore-forming processes.

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Translated by M. Moláková

Plate I

Figs. 1—2-Large scales of graphite, standard sample SL-1 (Sri Lanka) granulite facies; 1-X 450, 2-X 230 (SEM). Fig. 3-Cleavage pattern of graphite, sample SL-1, X 1400 (SEM). Figs. 4—5-Graphite scales, sample ČK-MV-1, Český Krumlov, Městský vrch — graphite deposit; amphibolite facies, 4-X 4500, 5-X 800, (SEM). Fig. 6-Partly hexagonal outlines of a graphite scale, sample G-1, Jasenie—Biela Voda, transition between biotite zone and amphibolite facies: X 4000 (SEM). Figs. 7—8-Various habits of graphite particles, sample HM-1 Biela Voda—Melicherka; biotite zone of the green schist facies; 7-X 1500, 8-X 900 (SEM).

Plate II

Fig. 1-Cleavage surface of graphite, sample HM-1, Biela Voda—Melicherka, biotite zone of the green schist facies; X 10 000 (SEM). Fig. 2-Distorted plate of graphite, borehole L-5 (106.9 m), Lomnistá dolina Valley biotite zone of the green schist facies; X 2300 (SEM). Figs. 3, 4, 5-Particles of graphite of various sizes and irregular outlines, borehole VNT-7 (81.5 m), Sopotnica Valley, transition between green schist and amphibolite facies: 3-X 2700, 4-X 1500, 5-X 1400 (SEM). Figs. 6, 7, 8-Various habits and sizes of graphite particles, one of them having almost perfect hexagonal form; borehole VNT-7b (133.3 m), Sopotnica Valley, transition between biotite zone and amphibolite facies; 6-X 2200, 7-X 3000, 8-X 6000 (SEM).

Plate III

Figs. 1—2-Graphite scales, partly with hexagonal outlines borehole VNT-11 (51.5 m) Sopotnica Valley, amphibolite facies; 1-X 2000, 2-X 3500 (SEM). Figs. 3, 4, 5-Partly hexagonal patterns of graphite borehole VNT-12 (14 m), Sopotnica Valley biotite zone of the green schists facies; X 10 000 (SEM). Fig. 6-Distorted plate of graphite with irregular on partly hexagonal habit, borehole VNT-13 (22—27 m) Sopotnica Valley transition between biotite zone and amphibolite facies; X 2500 (SEM). Fig. 7-Graphite particles with ragged outlines, borehole VNT-13 (22—27 m) Sopotnica Valley; X 2500 (SEM).

Plate IV

Fig. 1—8-Particles of graphitized carbonaceous matter; samples: G-8 (1), Suchá dolina Valley—Medveďová X 3000, MH-4 (2, 3) Biela Voda—Melicherka, 2-X 5500, 3-X 9000, MH-5 (4, 5, 6) Biela Voda—Melicherka, 4-X 4000, 5-X 7500, 6-X 10 000. MH-8 (7—8) Biela Voda—Melicherka, 7-X 5000, 8-X 8000 green schist facies; (SEM).

Plate V

Fig. 1-A part of graphite monocrystal with hexagonal outlines; visible extinction lines sample G-1, Biela Voda Valley, Melicherka, transition between biotite zone and amphibolite facies X 50 000 (TEM). Fig. 2-Graphite flakes with hexagonal and rounded outlines sample G-1, X 5000 (TEM). Fig. 3-Graphite particle with irregular outlines, sample VŽ-1, Malé Železnô, S slope of the Klinisko hill, biotite zone, X 10 000 (TEM). Fig. 4-Graphite particle with hexagonal habit, sample VŽ-1 Malé Železnô, X 13 000 (TEM). Fig. 5-Irregular flake of semigraphite (translucent to electron beam), bright field, sample G-3 Sovíansko—Haliar, biotite zone, X 7500 (TEM). Fig. 6-The same particle, dark field, technique, (TEM).

Plate VI

Fig. 1-SAD pattern of the particle shown on micrograph 5, Plate V. Figs. 2, 3, 4--Graphized carbonaceous matter with vestiges of microorganism (?), bright field, dark field and SAD pattern, sample G-5, Biela Voda—Majdačka; X 6000 (TEM). Figs. 5—6-A particle of nongraphitized carbonaceous matter, possibly a fragment of microorganism, bright field an SAD pattern exhibiting a diffuse ring, sample G-8, Suchá dolina, Medveďová Valley; X 10 000 (TEM).

Plate VII

Figs. 1—2-Carbonified relic of a microorganism, bright field and SAD pattern, showing elliptical rings, sample HE-1, N slope of Ráztocká hoľa hill, X 20 000 (TEM). Figs. 3—4-Carbonaceous particle with irregular outlines, sample HE-1, X 6600 (TEM). Figs. 5—6-Carbonaceous particle locally displaying crystalline outlines, sample HE-1; 5-X 5000, 6-X 8300 (TEM).

Plate VIII

Fig. 1-SAD pattern of the particle shown on the Fig. 6, Plate VIII. Figs. 2—3-Carbonaceous organic matter, bright field and electron diffractions pattern showing elliptical rings, sample HE-2, N slope of Ráztocká hoľa hill, X 10 000 (TEM). Figs. 4, 5, 6, 7-Particles of carbonaceous matter, may be fragment of a microorganisms, sample BU-1, Bukovecká dolina Valley; 4-X 10 000, 5-X 10 000, 6-X 8300, 7-X 10 000 (TEM).

Plate IX

Fig. 1-Particle of carbonaceous matter sample BU-1, Bukovecká dolina Valley, bright field, X 16 000 (TEM). Figs. 2—3-Carbonified fragment of a microfossil, bright field and SAD pattern with diffuse ring sample BU-1 Bukovecká dolina Valley; X 10 000 (TEM). Figs. 4, 5, 6-Carbonaceous particle, bright field, diffuse SAD pattern, and dark field, sample BU-5 Bukovecká dolina Valley; X 40 000 (TEM). Fig. 7-Fragment of carbonaceous matter, (solid bitumen?), sample BU-5, Bukovecká dolina Valley, X 12 000 (TEM).

Plate X

Figs. 1, 2, 3-Graphitized carbonaceous matter, bright field dark field and electron diffraction, sample BU-Bukovecká dolina Valley; X 10 000 (TEM). Figs. 4 5-Carbonaceous particle, bright field and diffuse SAD pattern, sample HE-1, northern slope of Ráztocká hoľa hill; 4-X 150 000 (TEM). Figs. 6, 7-Fragment of partly graphitized phytoclasts with inclusions of chromite (?) and gold (black dots), and synthetic SAD pattern; sample HE-1; 6-X 165 000, (TEM).

Plate I

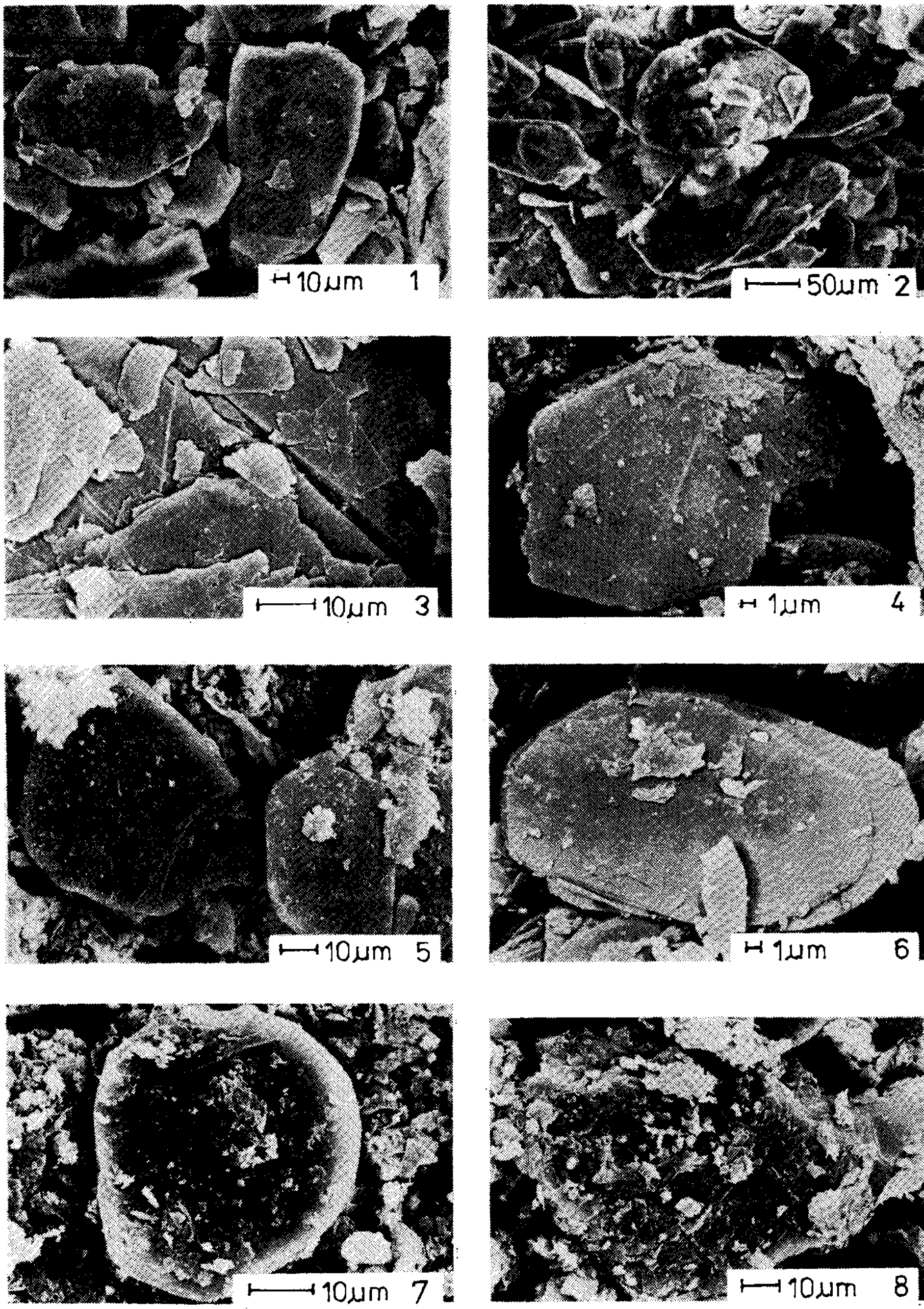
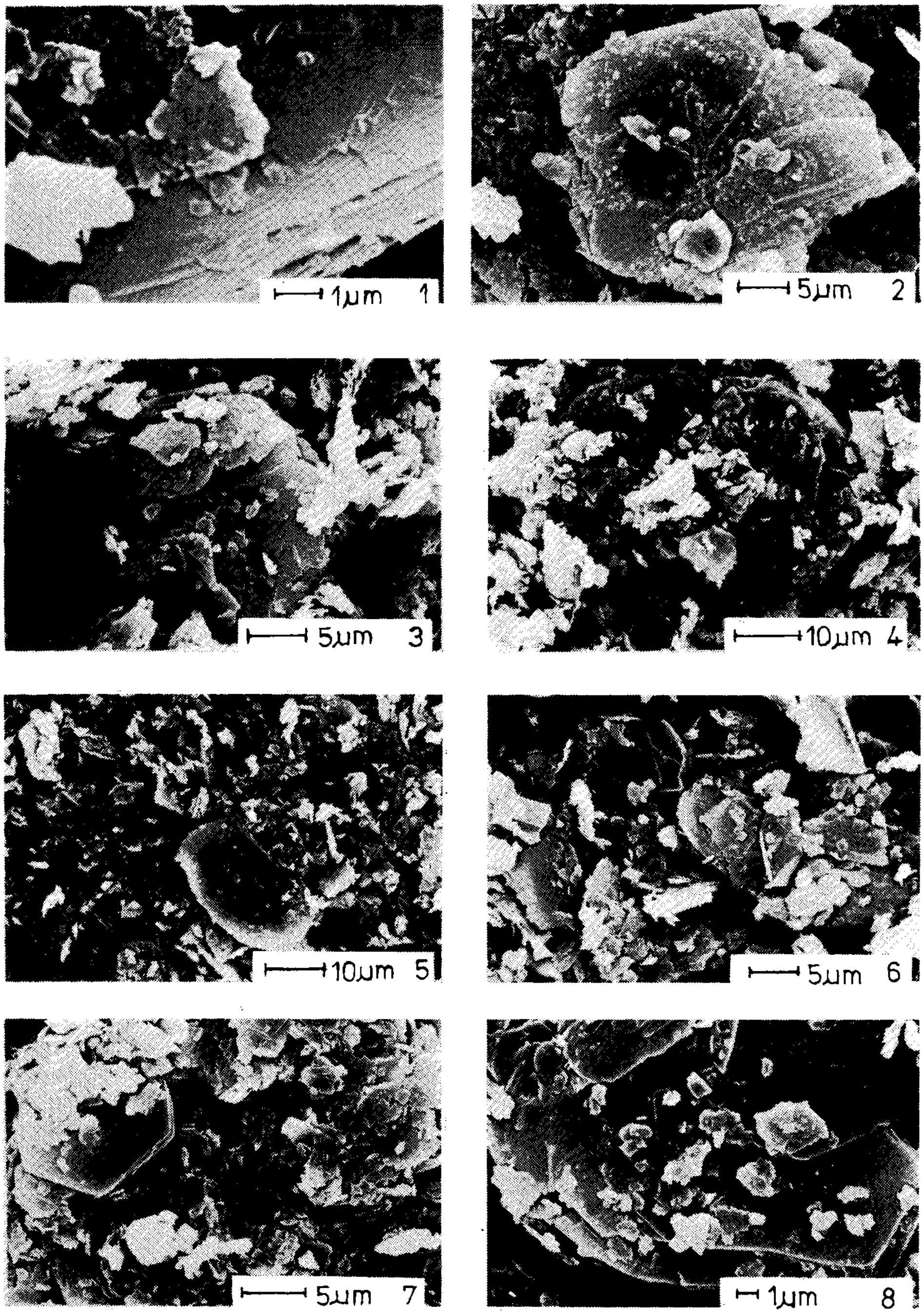


Plate II



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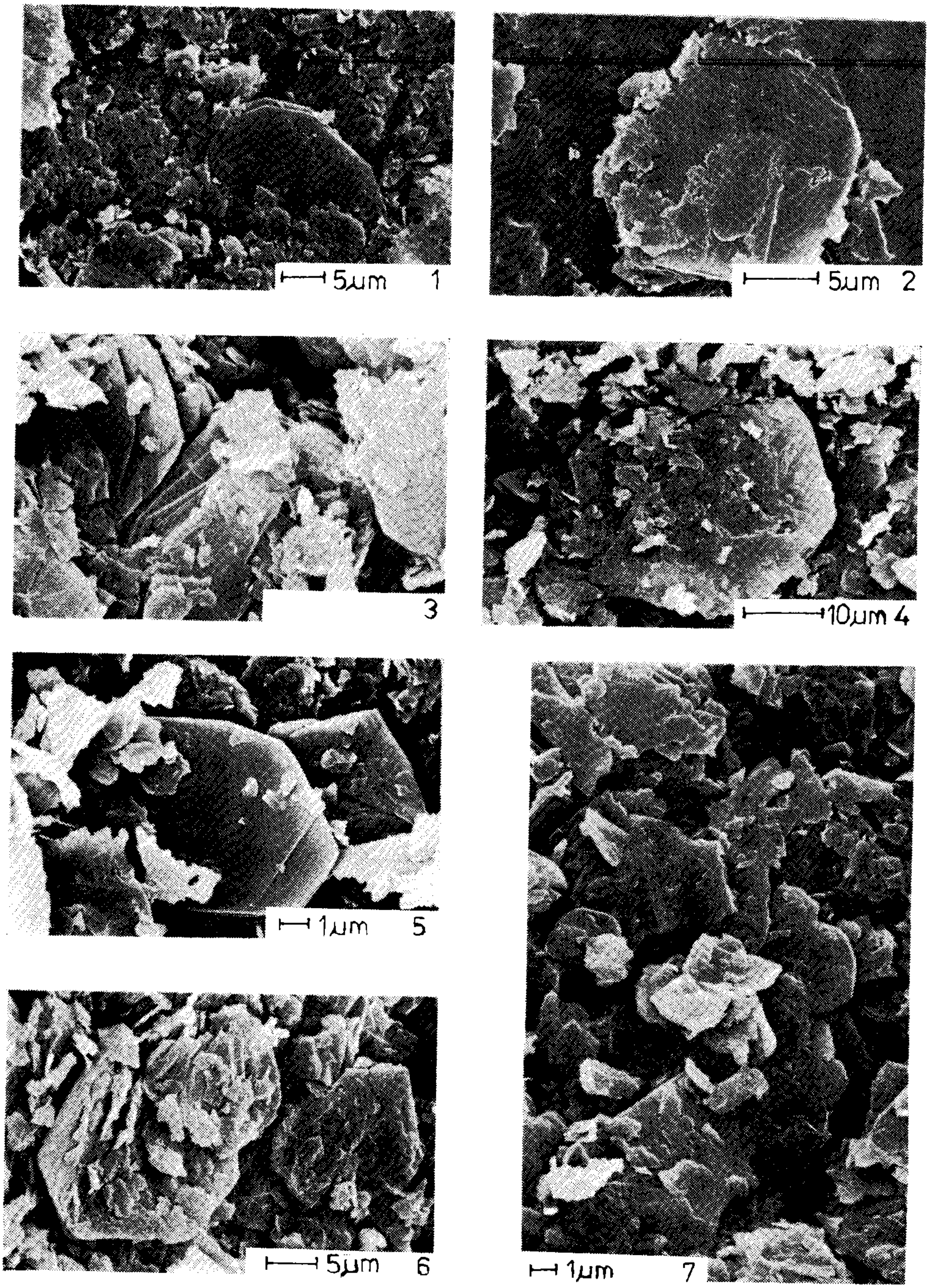

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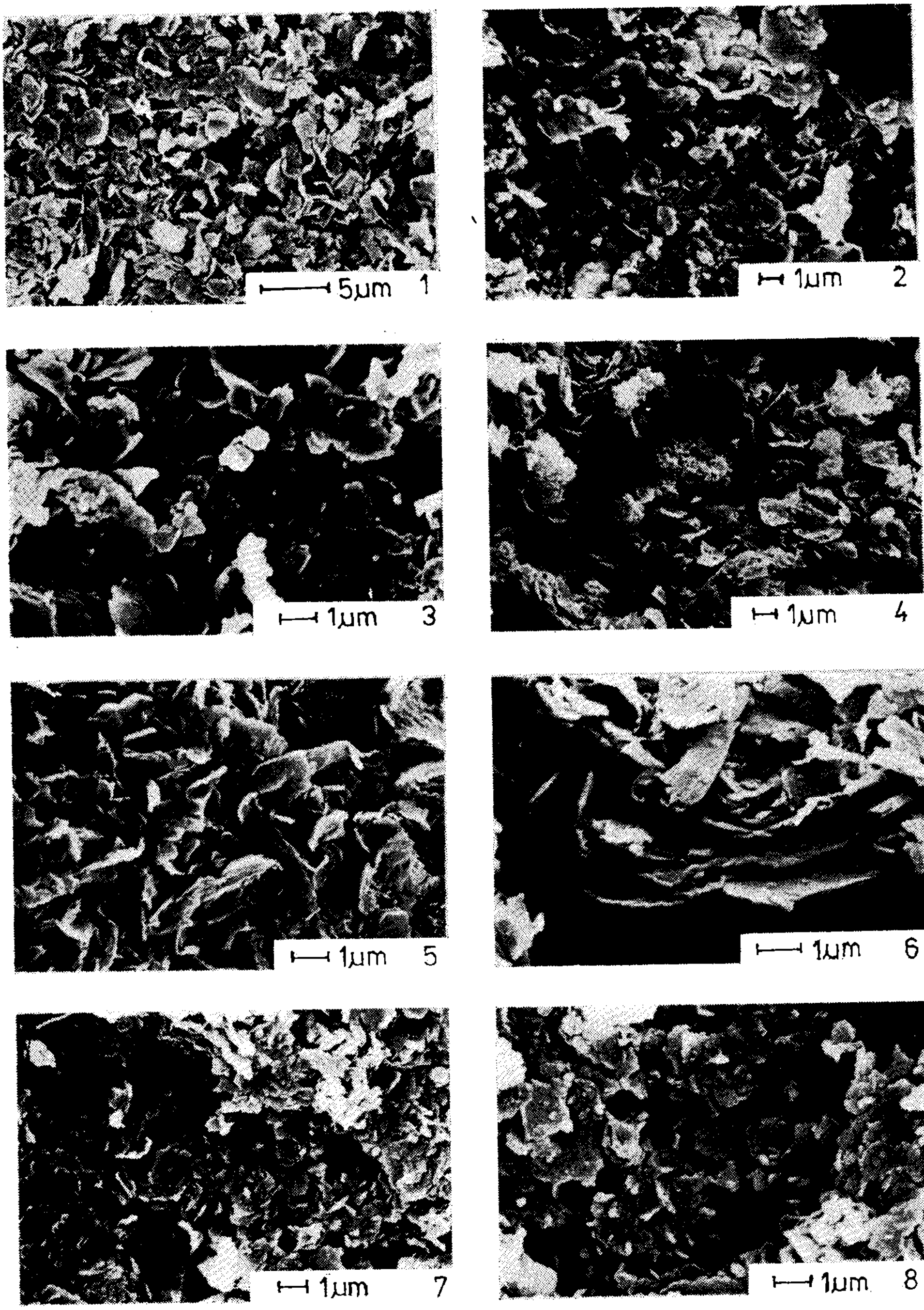

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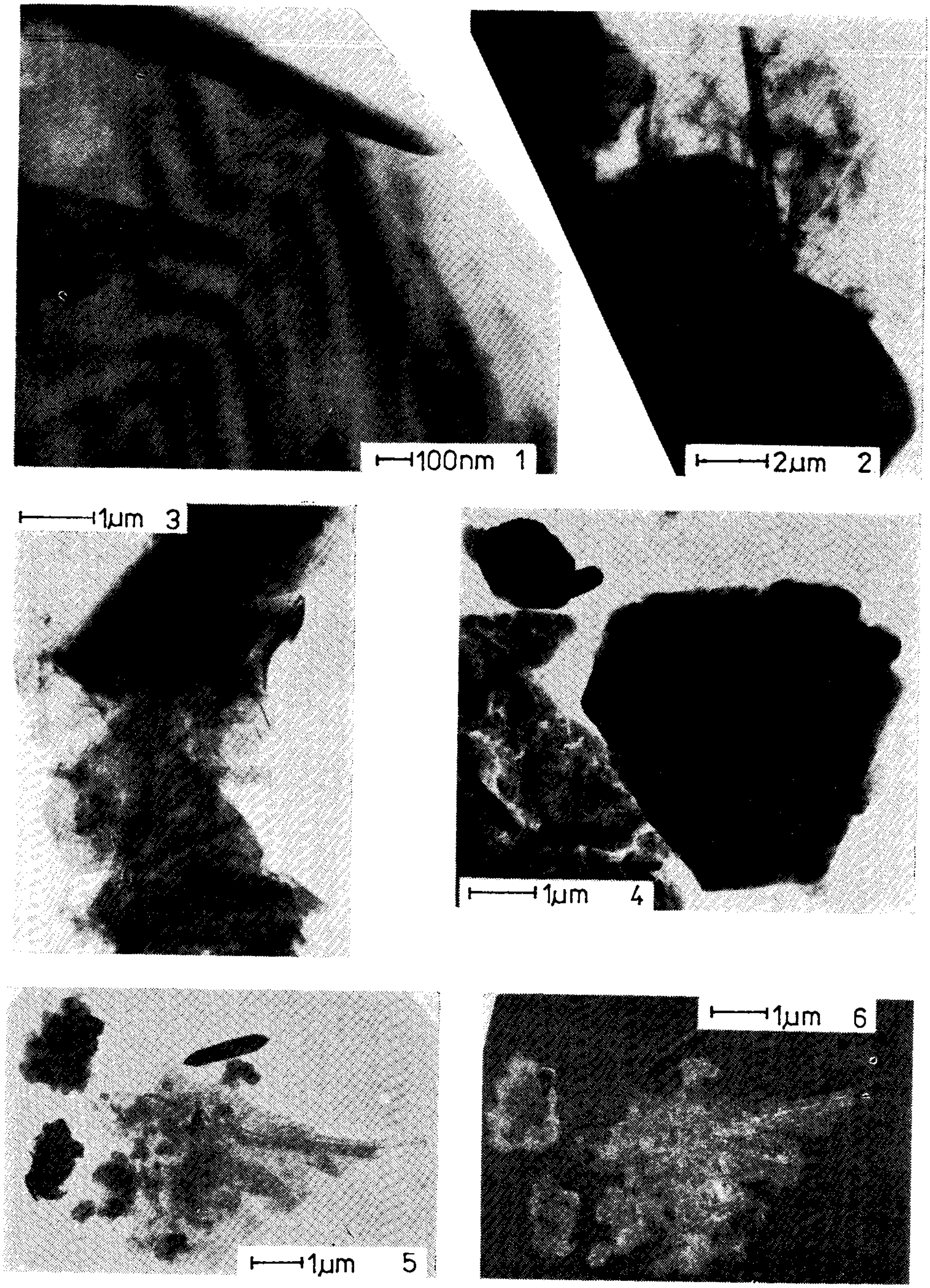

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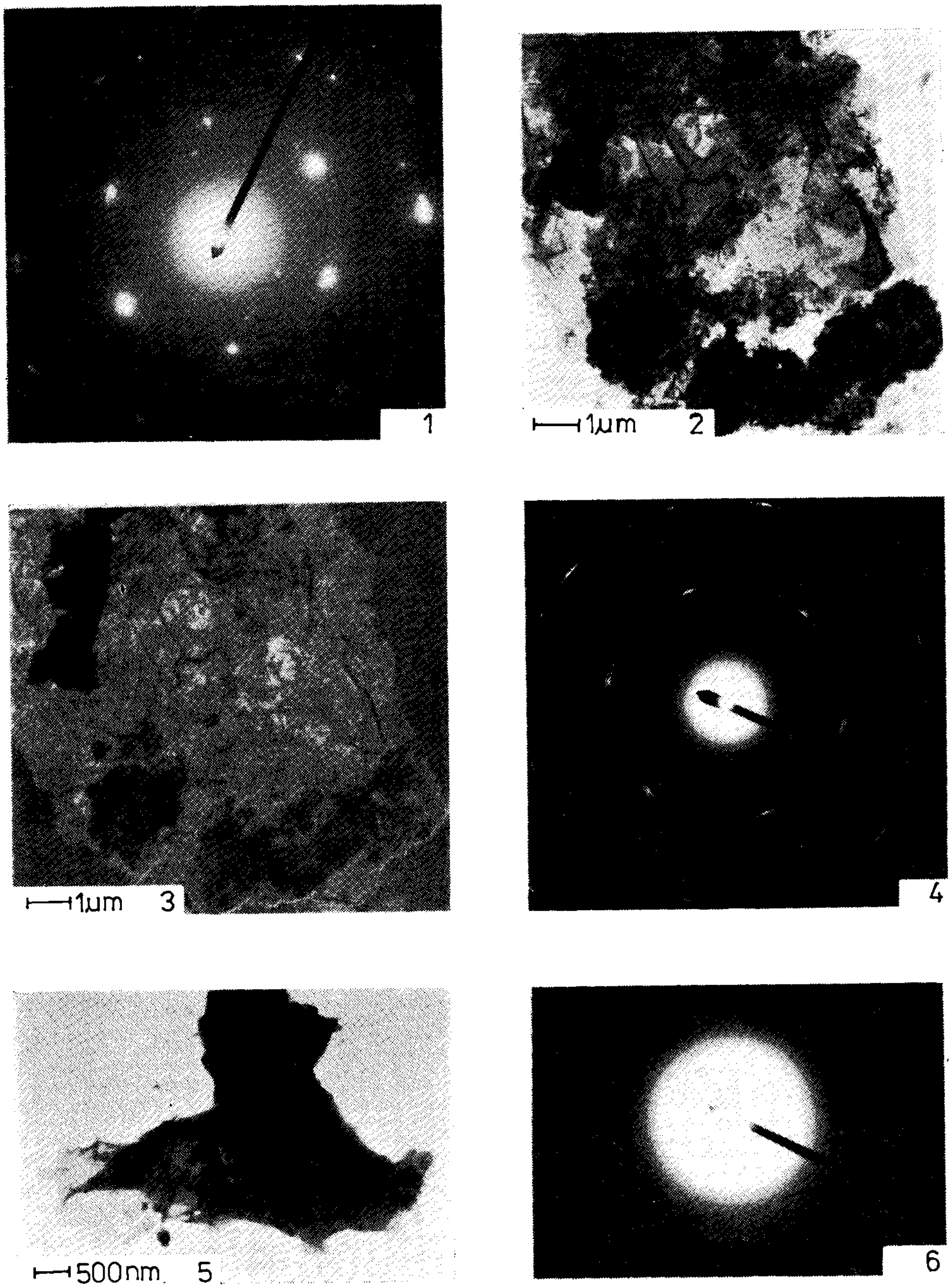

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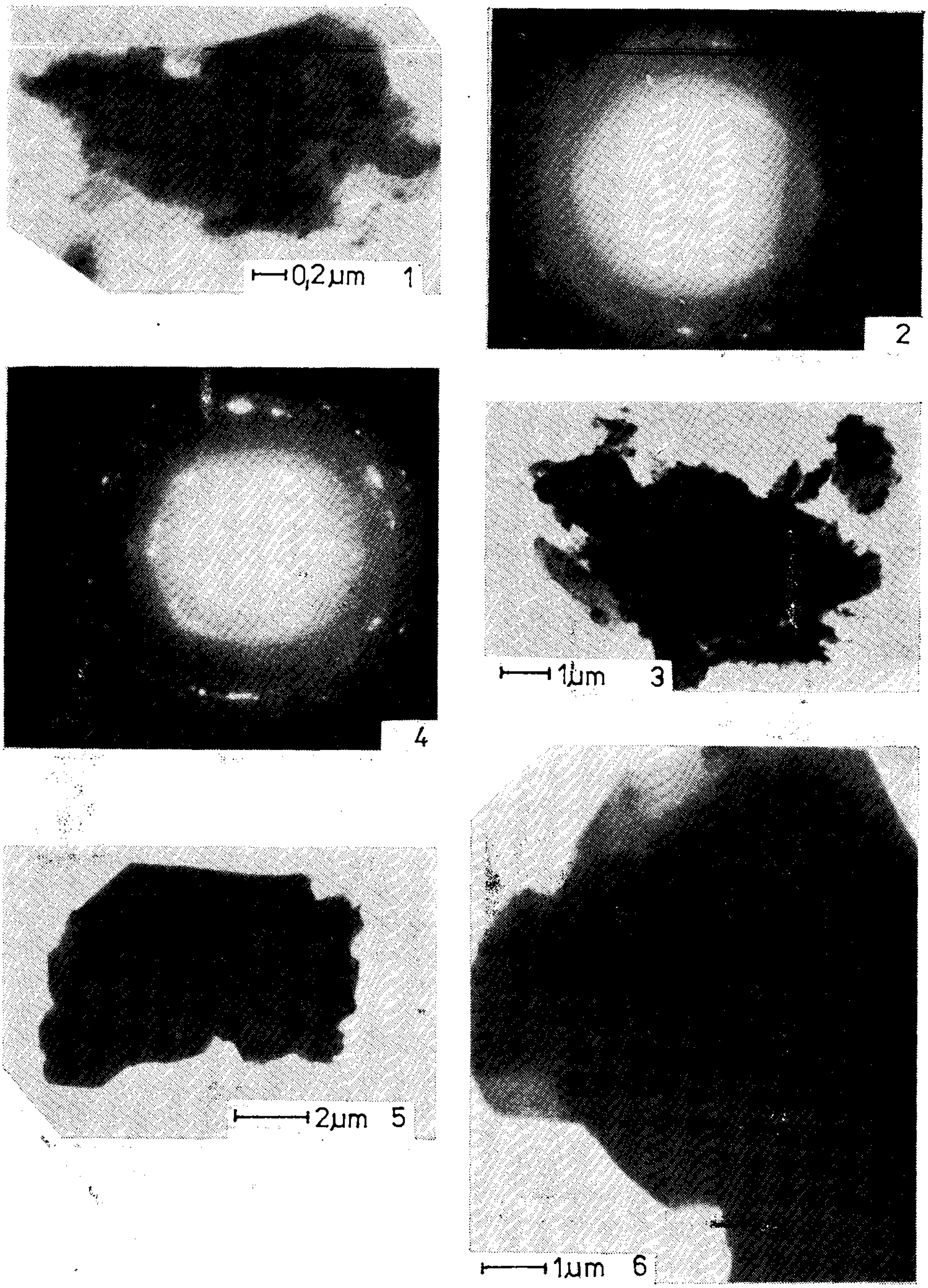

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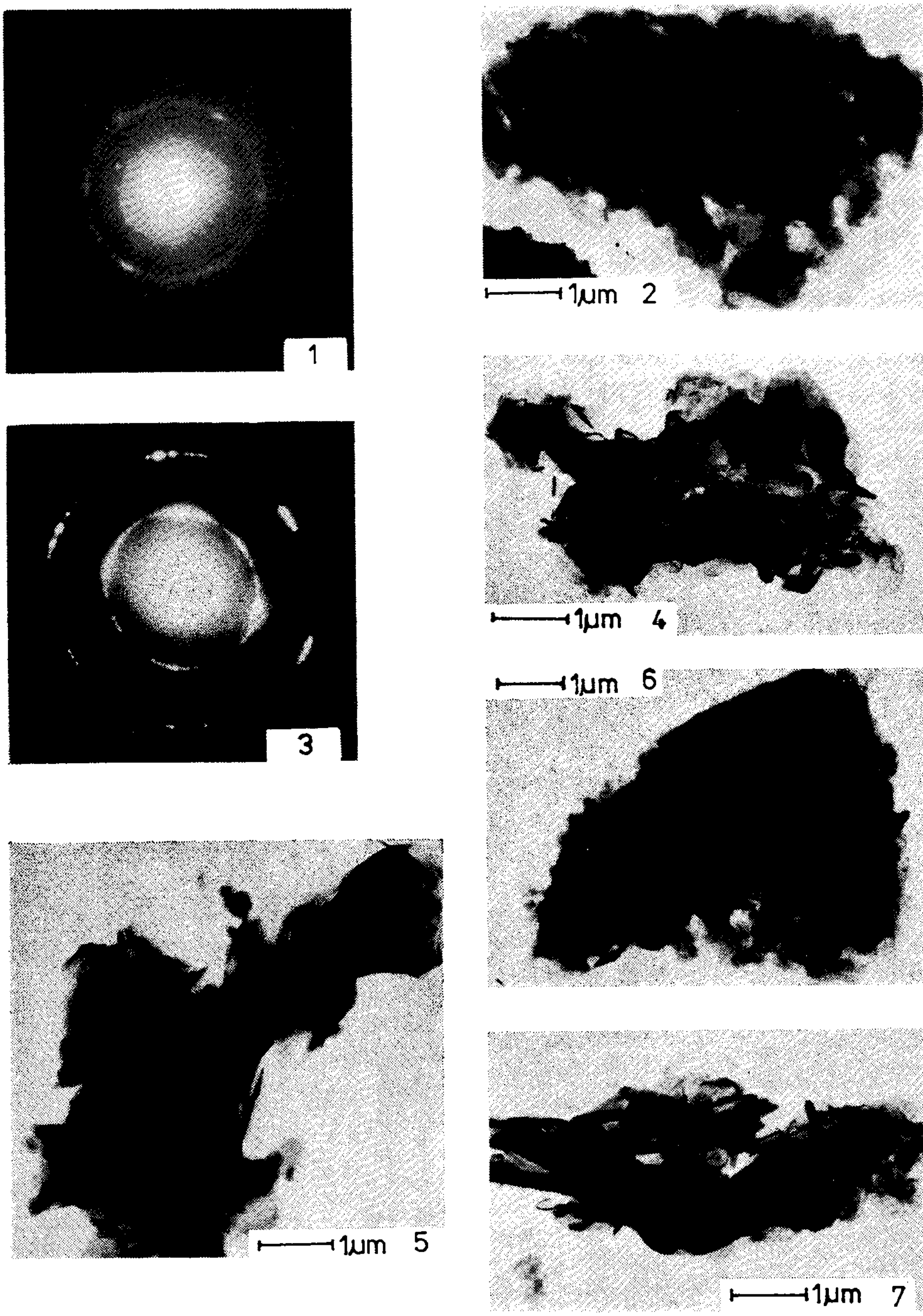


Plate IX

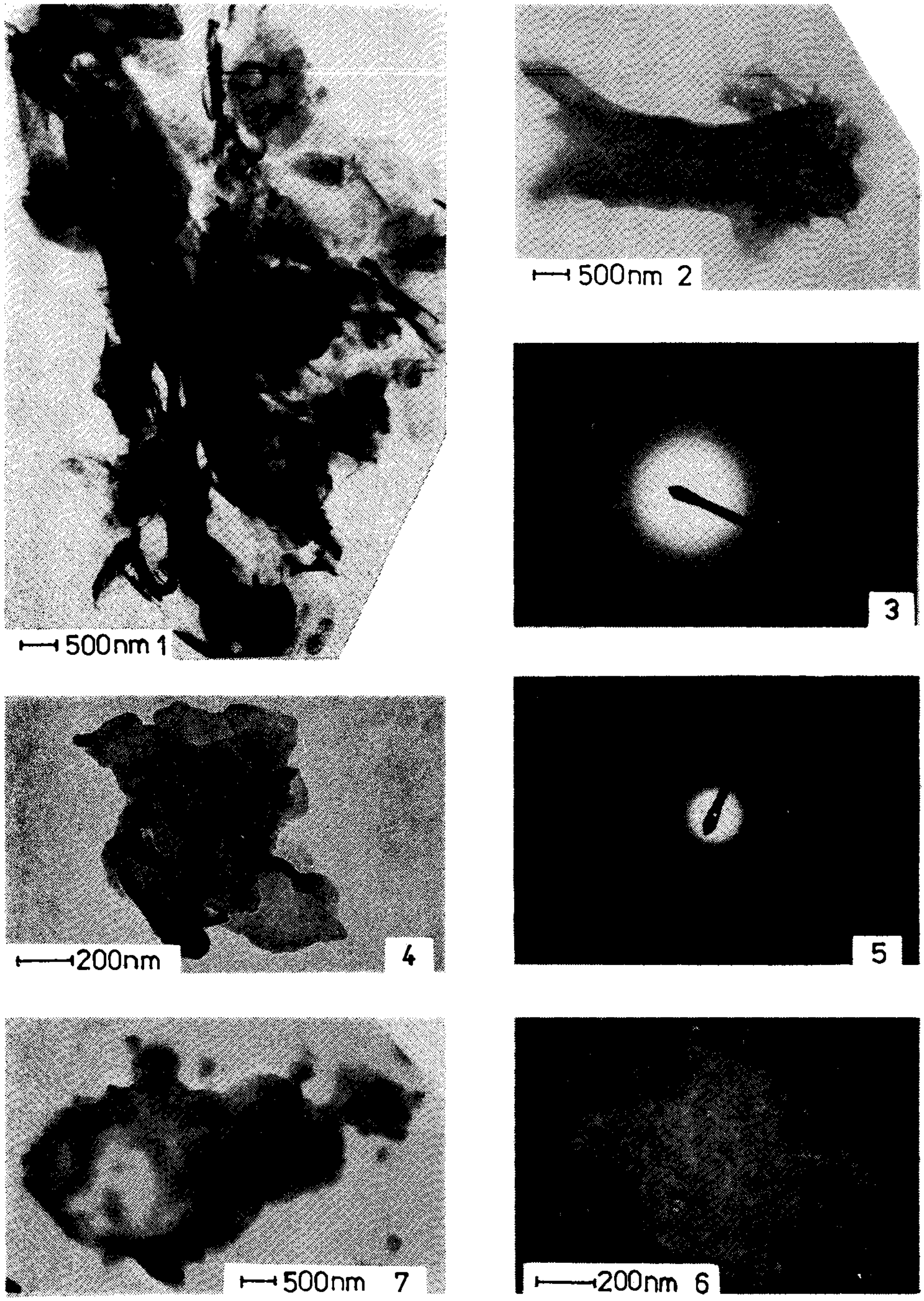
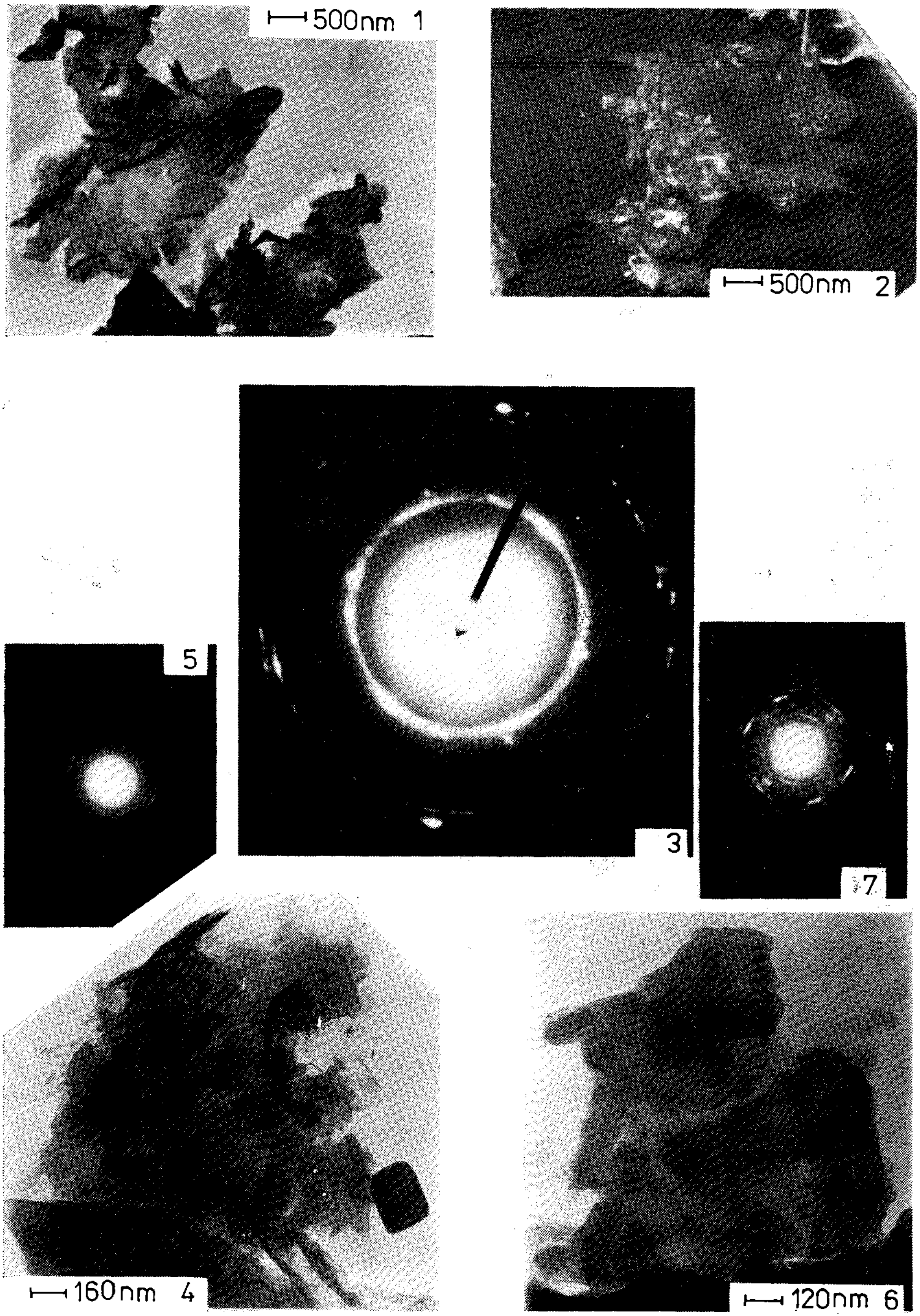


Plate X



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