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Stable isotope composition of carbon in selected carbonaceous units of Slovakia with reference to Úrkút (Hungary) and Copperbelt (Zambia) examples

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Abstract Although sufficient information exists on the isotope composition of carbonate carbon in several sedimentary rock units and mineral deposits of the Slovak Carpathians, no comprehensive isotopic study has yet been carried out on the reduced carbon found in carbonaceous units. To fill this gap authors have summarized and evaluated in this paper all available isotopic results and attempted to update the fragmentary information. Foreign reference samples, including those from Úrkút Mn ore deposit and Copperbelt Cu-Co district, have also been analyzed in order to compare the results and to contribute to resolution of some genetic aspects in the respective deposits. It is shown that most carbons are enriched in ^{12}C isotope and have organic matter as precursor. In a number of samples, however, pyrolitic reactions and/or re-equilibration between organic and carbonate carbon resulted in a shift to a more ^{13}C enriched variety. The intensity of re-equilibration depended mainly from the degree of metamorphism of the host rocks and availability of heavy carbon isotope in the process. The heavy carbon isotope could have been released from coexisting carbonates, or from "juvenile" sources. Relatively strong ^{12}C depletion has been observed in the samples collected from the shear zones, where organic carbon reacted with water, or a heavy carbon containing gas phase. The reaction with water lead to the formation of a ^{12}C enriched carbon oxide, leaving the original organic carbon, or graphite, relatively enriched in the heavy isotope. The most intense ^{13}C enrichment (average $\delta\ ^{13}C$ of -15.59 ‰) display the samples from the "Magnesite Carboniferous". Furthermore, the average δ values for Gemericum Unit are also less negative compared to the other major units of the Western Carpathian system, thus, authors propose a different paleoenvironmental development for this unit. Extreme enrichment in ^{13}C in one graphite sample (-8.66‰) indicates that it could have formed in a process of carbonate, or carbon dioxide reduction.

Key words: carbonaceous matter, stable carbon isotopes, evolutionary pathways, rock metamorphism, re-equilibration, origin of carbon, genetic considerations.

Introduction

This study has been motivated by almost complete lack of the carbon isotope data from the carbonaceous units of the Slovak Carpathians and an urge to attain a deeper insight into the genetic and metamorphic history of carbon in this important lithotype. In addition to the Slovakian samples, 16 foreign reference samples, out of which 10 come from the manganese deposit of Úrkút (Hungary) and the world known Cu/Co district of Copperbelt (Zambia), have also been assayed in order to compare the results from different environments and epochs, and to contribute to modelling genetic aspects of the respective mineral deposits.

The evaluation of results of this isotopic study has been preceded by an analysis of available literature concerned with stable carbon isotopes in the geological environment. Following lines are a review of available information and a summary of important features used in our interpretations.

The results of numerous isotope studies have shown that organic carbon found in geological materials is markedly enriched in the light isotope, while the heavy isotope associates with inorganic carbon, such as carbonate, bicarbonate or carbon dioxide. This is based on the fact that all pathways of biologic carbon fixation entail such types of isotope fractionation, which discriminate against ^{13}C and lead to preferential incorporation of the light carbon isotope into cell material. The $^{13}C/^{12}C$ ratios of both organic and carbonate carbon are preserved in sediments with but minor alterations though the ages, so the isotopic signature can be traced back to the beginning of the rock record (SCHIDLOWSKI in: JOHNS, 1986). A graphic summary of the isotope age functions of both carbon isotopes, spanning the time from Early Archean to present day, are shown in Fig. 1.

Isotopic changes, which take place during burial and diagenesis of organic matter are generally low, summing up to several permil over the maturation pathway, and never seriously obscure the isotopic signature of the primary biological material. The end product of the maturation process is kerogen - a polycondensed acid-insoluble carbonaceous residue, which contains slightly heavier carbon isotope relative to the progenitor material (SCHIDLOWSKI l.c.).

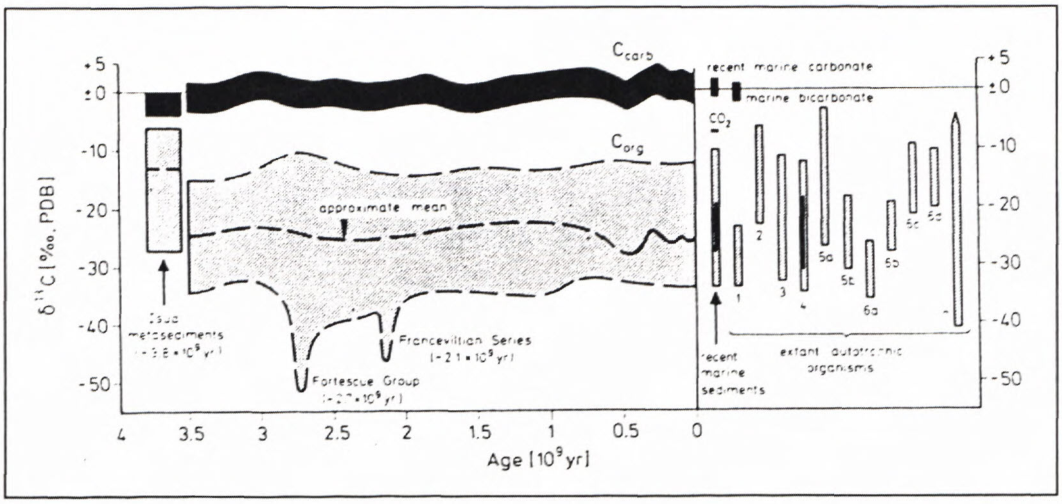


Fig. 1. Isotope age functions of sedimentary carbonate (C_{carb}) and organic carbon (C_{org}) as compared to the isotopic composition of their progenitors in the contemporary environments. Spreads shown for extant autotrophs are those of: 1) C_3 plants; 2) C_4 plants; 3) CAM plants; 4) eucaryotic algeae; 5) cyanobacteria from (a) natural communities and (b) culture experiments; 6a-d) non-oxygenic photosynthetic bacteria (Chromatiaceae, Rhodospyrillaceae, Chlorobiaceae, Chloroflexaceae); 7)chemoautotrophic bacteria (methanogens). After SCHIDLOWSKi (in: JOHNS 1986).

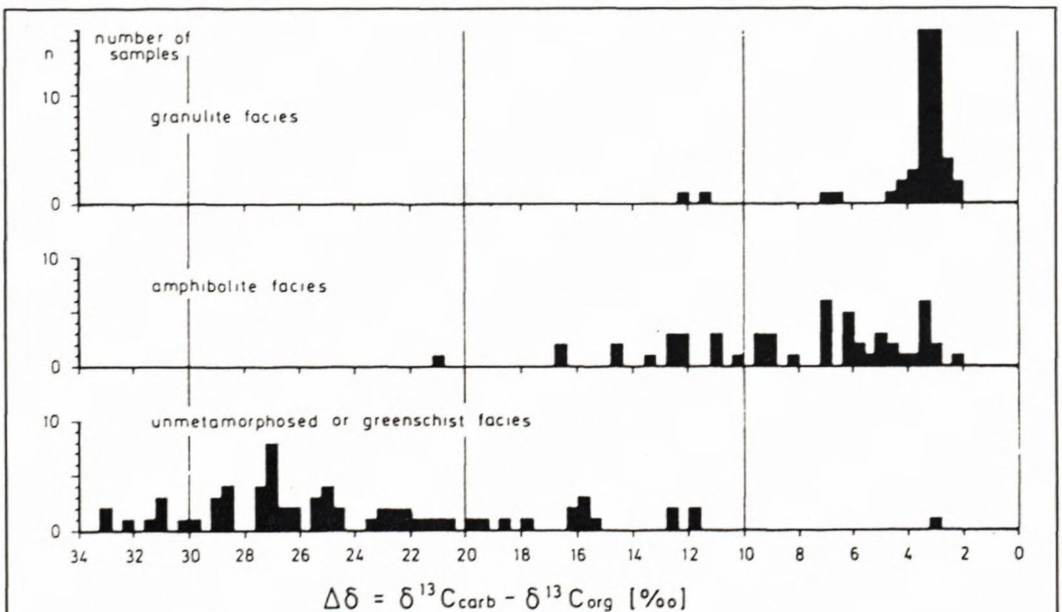


Fig.2. Isotopic re-equilibration between coexisting sedimentary carbonate (calcite) and organic carbon in response to rock metamorphism. The exchange is caused by mobilization of "heavy" CO_2 during decarbonation of primary carbonate rocks, which commences in the green schist facies (300-450 °C), becomes rather pronounced in amphibolite-grade rocks (450-650 °C) and thermodynamic re-equilibration is almost attained in the granulite facies (≥650 °C). After VALLEY and O'NEIL (1981).

Much more important are isotopic changes brought about by rock metamorphism. Temperatures exceeding 400 °C initiate pyrolitic reactions in primary organic matter, accompanied by release of CO_2, carbohydrates and water and by progressive carbonification (ANDREAE 1974). Escape of methane, CO_2 and other volatiles, enriched in ^{12}C, results in relative enrichment in ^{13}C isotope in the carbonaceous matter (CM).

Further changes take place due to re-equilibration with the heavy carbon. While the metamorphic alterations of the $^{13}C/^{12}C$ ratios in carbonate-fee rocks are negligible, isotopic re-equilibration between CM and coexisting carbonates at increased metamorphic conditions shifts the $\delta^{13}C$ values of carbon from around -26 to -10 ‰, or even more positive ones (SCHIDLOWSKI l.c.). This shift is caused by $^{13}C/^{12}C$ exchange with isotopically heavy CO_2 released from carbonates during metamorphic decarbonation reactions which start in the lower green schist facies and increase with metamorphic grade (VALLEY and O'NEIL 1981). As a function of metamorphic grade, the magnitude of fractionation between C_{org} and C_{carb} becomes progressively smaller, with equilibrium closely approached in the granulite facies (BOTTINGA 1969). Fig. 2 displays the variations in isotopic composition between coexisting calcite and organic carbon in response to increasing rock metamorphism (VALLEY and O'NEIL 1981).

Considerable isotopic changes occur in CM contacted with hydrothermal fluids. In such cases carbon equilibrates with ^{12}C depleted CO_2, contained in the fluid, or with water to form ^{12}C enriched CO gas and to leave the outcoming carbon relatively reacher in heavy isotope.

Another process shifting the original isotopic composition of reduced carbon to more positive values is associated with the presence of uranium in the system and the resulting interaction of α-particles with the organic matter. LANDAIS et al. (1990) reported a 10 ‰, deviation of $\delta^{13}C$-value in rocks containing 2 to 11.5% of U. On the other hand, LEWAN and BUCHARDT (1989) did not observe any effect on the carbon isotope composition of organic matter from uranium concentrations below 500 ppm.

Application of carbon isotope studies

The isotopic composition of reduced carbon have been studied by a number of authors worldwide with the objective to:

- find biological markers in the rocks (e.g. SCHIDLOWSKI in: JOHNS 1986),
- study the variations in carbon isotope composition through geological time (e.g. GALIMOV in: DURAND 1980, VEIZER et al 1980),
- assess metamorphic temperatures from the degree of isotopic exchange between carbonates and reduced carbon (e.g. BOTTINGA 1969, VALLEY and O'NEIL 1981),
- solve other geological tasks.

In order to correlate our results with more generalized data, we present below the following scheme of KROPOTOVA et al. (1976). From literature, they classified carbon isotopic data for graphites and graphitoide materials found in various geological environments into three ranges:

1. graphites in carbonatites with $\delta^{13}C$-values from -6 to -3 ‰,
2. mantle derived graphite from kimberlite pipes with $\delta^{13}C$-values from -10 to -7 ‰ and
3. graphite characterized by the composition of organic carbon with $\delta^{13}C$-values from -25 to -30 ‰.

Correlation of our isotopic data (see Table 1) with this scheme shows that the majority of them fall within the range of the third group. However, a shift to less negative values can be observed in several samples, indicating the presence of processes leading to incorporation of various amounts of heavy carbon. These processes could either be acquired in the primary sedimentary and/or diagenetic stages or, what is more important, by subsequent metamorphic re-equilibration reactions with the carbonate, the juvenile carbon, or with water. As the contents of uranium in our samples are considerably lower than 500 ppm, we cannot expect any significant effects of α-particles upon the isotopic composition of the CM.

Some of our reference samples can be used as examples to demonstrate the re-equilibration processes related to metamorphism (Table 1).

The first example is C-1 sample of carbonaceous marble exposed to a medium grade metamorphism, which resulted in a re-equilibration of the CM with carbonate carbon and a reduction of the $\delta^{13}C$ value to 40-50 % of its original value.

A similar degree of re-equilibration has been achieved in the SL-1 graphite due to a reaction with juvenile carbon in a gaseous phase. This process occurred under metamorphic conditions of granulite facies.

The SF-1 sample is a tuff intercalated with dolomite metamorphosed under conditions of amphibolite facies. In this case the reduction of $\delta^{13}C$-value due to the re-equilibration with a carbonate or a gaseous carbon phase changed the original carbon isotope composition by some 40% .

Table 1 Stable isotope composition of carbons

SAMPLE	TYPE	ROCK	AGE	LOCALITY	UNIT	TOC	ISOTOPE-C
G-1	G	black schist	Lower Paleozoic	Jasenie, Melicherka	TNT	1.00	-25.13
G-3	SG	black schist	Lower Paleozoic	Jasenie, Soviansko	TNT	0.97	-30.46
G-4	SG	grey schist	Lower Paleozoic	Jasenie, Biela voda, Viržing	TNT	0.09	-24.51
G-5	G	grey schist	Lower Paleozoic	Jasenie, Biela voda, Viržing	TNT	0.06	-27.46
G-7		grey schist	Lower Paleozoic	Jasenie, Kyslá, Čremošnô	TNT	0.11	-24.92
G-8	SG	grey schist	Lower Paleozoic	Jasenie, Suchá, dol. Medveďová	TNT	0.12	-22.06
G-9	SG	grey schist	Lower Paleozoic	Sopotnická dol. Ramženô	TNT	0.16	-22.60
HE-1	MA	grey schist	Lower Paleozoic	Jasenie, Hor. Erenštanka	TNT	0.13	-23.10
HE-1	MA	grey schist	Lower Paleozoic	Jasenie, Hor. Erenštanka	TNT		-22.89
HE-2	MA	grey schist	Lower Paleozoic	Jasenie, Hor. Erenštanka	TNT	0.07	-23.46
HM-1a	SG	grey schist	Lower Paleozoic	Jasenie, Hor. Erenštanka	TNT		-25.26
HM-5	SG	grey schist	Lower Paleozoic	Jasenie, Hor. Erenštanka	TNT	0.35	-25.80
HM-8		grey schist	Lower Paleozoic	Jasenie, Melicherka	TNT	0.10	-27.49
HM-9		grey schist	Lower Paleozoic	Jasenie, Melicherka	TNT	0.13	-25.57
HUS-5		mylonite + graphite	Lower Paleozoic	Jasenie, Husárka	TNT		-18.89
MAT-1	G	gneiss + graphite	Lower Paleozoic	Bukovec, Pod Matúšovou	TNT	0.45	-30.72
MAT-2	G	quartz.gneiss + graphite	Lower Paleozoic	Bukovec, Pod Matúšovou	TNT	0.08	-28.97
MEDZ-1	G	phyllonite + graphite	Lower Paleozoic	Medzibrod-Močiar, dump	TNT	0.46	-28.78
MEL-21	MA	2-mica.schist + graphite	Lower Paleozoic	Jasenie, Melicherka	TNT	0.10	-27.84
NT-1	G	granitoide + graphite	Lower Paleozoic	Jasenie, Gelfúsová (Štefan adit)	TNT		-24.10
NT-6/2	G	paragneiss + graphite	Lower Paleozoic	Jasenie, Gelfúsová (Štefan adit)	TNT		-18.60
SOV-1		black shale	Lower Paleozoic	Jasenie, Sova-Haliar	TNT		-25.88
SOV-2	SG	mylonite + graphite	Lower Paleozoic	Jasenie, Sova-Haliar	TNT	0.24	-20.60
V-1 (419.5 m)		2-mica schist + graphite	Lower Paleozoic	Jasenie, Prostredná dol., Bauková	TNT	0.01	-25.12
VNT-11 (81-92)	G	graphitic schist	Lower Paleozoic	Sopotnická dol. valley	TNT	0.32	-29.66
VNT-12 (14 m)	SG,G	graphitic schist	Lower Paleozoic	Sopotnická dol. valley	TNT	0.34	-28.50
VNT-12 38.5 m)	G	graphitic schist	Lower Paleozoic	Sopotnická dol. valley	TNT	0.90	-29.54
VNT-12 (96 m)		graphitic schist	Lower Paleozoic	Sopotnická dol. valley	TNT	0.10	-28.38
VNT-13 (22-27 m)	SG,G	graphitic schist	Lower Paleozoic	Sopotnická dol. valley	TNT	0.40	-28.19
VNT-14 (101-112 m)		graphitic schist	Lower Paleozoic	Sopotnická dol. valley	TNT	0.10	-24.49
VNT-14 (24-33 m)		graphitic schist	Lower Paleozoic	Sopotnická dol. valley	TNT	0.10	-25.24
VNT-15 (114-115,8 m)	G	graphitic schist	Lower Paleozoic	Sopotnická dol. valley	TNT	1.85	-26.33
VNT-15 (179 m)	G	graphitic schist	Lower Paleozoic	Sopotnická dol. valley	TNT	0.40	-27.91
VNT-15 (235-236,5 m)	SG,G	graphitic schist	Lower Paleozoic	Sopotnická dol. valley	TNT	0.10	-27.02
VNT-15 (235-236.5 m)	SG,G	graphitic schist	Lower Paleozoic	Sopotnická dol. valley	TNT		-29.63
VNT-7 (81.5 m)	SG,G	graphitic schist	Lower Paleozoic	Medzibrod, Močiar, drill hole	TNT	0.97	-30.26
VNT-7B (133.3 m)	SG,G	graphitic schist	Lower Paleozoic	Medzibrod, Močiar, drill hole	TNT	0.64	-28.93
VPB-5 (194.5 m)		grey schist	Lower Paleozoic	Bukovec, near E of SNP memorial	TNT		-27.44
VŽ-1	G,MA	schist+graphite	Lower Paleozoic	V. Železnô, pod Kliniskom	TNT	0.13	-29.43
Š-3, MB 100,75 m S		dark schist	Lower Paleozoic	Jasenie,Š-3 adit,75 m S of SP100	TNT	0.01	-27.42
P-24	G	granitoide	Variscan	Malá Fatra Mts. (Lúčna part)	TMF		-23.50
P-39	G	granitoide	Variscan	Malá Fatra Mts. (Lúčna part)	TMF		-24.30
P-45/1	G	aplite	Variscan	Malá Fatra Mts. (Lúčna part)	TMF		-19.00
P-53	G	pegmatite	Variscan	Malá Fatra Mts. (Lúčna part)	TMF		-22.60
P-60/2	G	paragneiss	Variscan	Malá Fatra Mts. (Lúčna part)	TMF		-25.70
AUG-1	SA	black shale	Lower Paleozoic	Pezinok, Augustín adit	TMK		-30.30
52/75	G	graphitic schist	Lower Paleozoic	Ostrica, slope S of trig. p. 684 m	TSM	0.90	-32.88
NEVIDZ.-1	G	graphitic phyllonite	Lower Paleozoic	Nevidzany, cca 1 km S from vill.	TSM	1.99	-32.25
JEŽ-1	G	q. -biot. gneiss+graphite	Lower Paleozoic	Bujakovo, nad Ježovou	VEP		-28.39
KS-1 (154,6 m)	SG	bi. -alb. gneiss+graphite	Lower Paleozoic	Klenovec, d. h. KS-1	VEP	0.05	-8.66
KS-1 (237,5 m)	SG	bi. -alb. gneiss+graphite	Lower Paleozoic	Klenovec, d.h. KS-1	VEP	0.40	-30.99
KI-108/86	SG	garnet. schist+graphite	Lower Paleozoic	Klenovec, 500 m N from Hôra	VEP	0.12	-23.38
KI-42/86	SG	garnet. schist+graphite	Lower Paleozoic	Klenovec, 2 km N of Pavlínka	VEP	0.51	-27.42
BAC-1/R	SG	grey schist	Lower Paleozoic	Bacúch, Ramžová dolina valley	VEP	0.37	-23.70
BYS-2		black schist	Lower Paleozoic	confluence Bystr. & Štiavnička	VNT	0.23	-26.22
JAN-1		grey schist	Lower Paleozoic	Jančíkova dol. valley	VNT		-28.71
KLI-1		black schist	Lower Paleozoic	Bystrá, Bystr. & Štiav. confluence	VNT		-29.80
POL-1	SG	q. phyllite+graphite	Lower Paleozoic	Polomka, P. & Ľ. Ráztoka confl.	VNT	2.50	-32.60
DB-252	MA	vein-quartz+stib.+graph	Lower Paleozoic	Spiš. Baňa (Sb), Margita, dump	GE		-26.70
DB-488	A	vein-quartz+stib.+graph	Lower Paleozoic	Čučma (Sb), Rozália adit, dump	GE		-24.69
MG-1		black shale	Lower Paleozoic	N. Slaná Mine (Fe)	GE		-23.33
NS-1		black shale	Lower Paleozoic	Nižná Slaná Mine, IX. horizon	GE		-24.62
NS-2	SA	black shale	Lower Paleozoic	N. Slaná Mine, Manó, X. horizon	GE		-26.61
S-1	A	black shale	Lower Paleozoic	Smolník, d. h. Rb-3 (87 m)	GE		-27.25
B-1	SA	black shale	Lower Paleozoic	Brádno (Slov. Nat. Museum)	GSZ		-23.54
KAD-1		black shale	Lower Paleozoic	Kadlub (relinguish. graphite mine)	GSZ		-21.79
Ro-3 (101-101,5 m)	MA	black shale	Carboniferous	Rochovce, d.h. Ro-3	GSZ	1.10	-20.71
Ro-3 (133,2 - 133,4 m)	SG	black shale	Carboniferous	Rochovce, d.h. Ro-3	GSZ	1.40	-19.96
Ro-3 (190-191 m)		black shale	Carboniferous	Rochovce, d.h. Ro-3	GSZ		-22.71
Ro-3 (75,3-76,7 m)	MA	black shale	Carboniferous	Rochovce, d.h. Ro-3	GSZ	1.34	-21.03
Ro-4 (155,4 m)		black shale	Carboniferous	Rochovce, d.h. Ro-3	GSZ	0.80	-23.43
16 b/IV		black shale	Carboniferous	Burda, III. hor. 50 m S from N. Adit	GMC		-13.83
32 b/VI		black shale	Carboniferous	Burda, III. hor. 50 m S from N. Adit	GMC		-17.30
33 b/IV		black shale	Carboniferous	Burda, III. hor. 50 m S from N. Adit	GMC		-14.29

SAMPLE	TYPE	ROCK	AGE	LOCALITY	UNIT	TOC	ISOTOPE-C
Pb 30b/72		black shale	Carboniferous	Podrečany, open pit (magnesite)	GMC		-17.40
Pb 30a/72	A	black shale	Carboniferous	Podrečany, open pit (magnesite)	GMC		-15.11
DRŽ-1/2 (90,5-90,8 m)	A	black shale	Jurassic	Držkovce, d.h. DRŽ-1	SIL	0.60	-27.46
DRŽ-1/7 (700,4-700,5 m)	SA	black shale	Jurassic	Držkovce, d.h. DRŽ-1	SIL	0.50	-24.84
N-2 (3447 m) (HF,GCL)	SA	anthracit coal	Carboniferous	Nemčičky, drill hole N-2	K		-24.73
JŠ-1	SG	coal in andesite	Miocene	B. Štiavnica, N schaft, 2. h., Bieber	NV	13.62	-22.60
PŘI-1	G	pegmatite + graphite	Variscan	Přibyslavice	CZM		-29.44
VT-1	G	graphitic schist	Lower Paleozoic	Velké Třesné (Slov. Nat. Museum)	CZM		-25.29
ČK-MV	G	graphitic gneiss	Precambrian	Č. Krumlov, Městský vrch hill	CZM	18.00	-21.93
C-1	G	marble + graphite	Jurassic	Rincón Naranjo, Z. Trinidad, Cuba	CUB		-8.62
SL-1	L	graphite semitreated	Precambrian	Sri Lanka (graphite concentrate)	SL	95.00	-7.21
UR-162	L	black shale + Mn	Toarcian	Úrkút (Hungary), open pit	U	2.63	-30.78
UR-165	L	black shale + Mn	Toarcian	Úrkút (Hungary), open pit	U	4.56	-31.20
UR-172	L	black shale + Mn	Toarcian	Úrkút (Hungary), open pit	U	3.09	-30.29
UR-176	L	black shale + Mn	Toarcian	Úrkút (Hungary), open pit	U	3.35	-29.42
UR-OP-1	G	black shale + Mn	Toarcian	Úrkút (Hungary), open pit	U	5.65	-31.97
SF-1	G	graphitic tuff (Finland)	Precambrian	Vihanti, Hauterämi O/B + 460	V	1.53	-14.02
KAN-2	SG	black schist (Zambia)	Precambrian	Kansanshi open pit, S wall	Z	1.33	-24.62
MUF-GW/1	G	greywacke (Zambia)	Precambrian	Mufulira, "B" O/B, 60 MP2, 895 mL	Z	0.10	-23.92
NCHA-1	SG	black schist (Zambia)	Precambrian	Nchanga OP, 217 mL, 12E, S wall	Z	5.63	-22.73
S-15123	G	greywacke (,) (Zambia)	Precambrian	Muf. 43MP8, 895mL + 60 N, "B"O/B	Z	2.16	-27.34
X-680		black schist(Zambia)	Precambrian	Mufulira, 56P4,880 mL, 40S, "A" O/B	Z	1.34	-27.02

Caption to Table 1: Most column headings are selfexplanatory. The abbreviations in the second column are explained in the chapter on carbon modifications and those in the fifth column stand for: TNT- Nízke Tatry Mts., Tatricum Unit; TMF-Malá Fatra Mts., Tatricum Unit; TMK-Malé Karpaty Mts., Tatricum Unit; TSM-Suchý and Malá Magura Mts., Tatricum Unit; VEP-Southern part of Veporicum Unit; VNT- Nízke Tatry Mts., Veporicum Unit; GE-Gemericum Unit; GSZ-Zone of contact between Veporicum and Gemericum Units; GMC-"Magnesite Carboniferous", Gemericum Unit; SIL-Meliaticum Unit; K-Carboniferous, Inner flysch basement; NV-Neovolcanic rocks; Foreign samples: CZM-Czech massif; CUB-Cuba, Escambray; SL-Sri Lanka; U-Úrkút, Hungary; V-Vihanti mine, Finland; Z-Zambian Copperbelt. TOC - total organic carbon.

The smallest re-equilibration, to 80-90% of its original value, experienced the graphite in the sample ČK-MV (Fig.9a). Although the gneissic host rock was here exposed to amphibolite facies metamorphism and carbonates do occur within the area of this deposit, the intensity of re-equilibration process was limited due to unknown reasons.

Our presumption that the degree of re-equilibration under contact metamorphic conditions should be considerably smaller compared to that attained under regional conditions can be supported by observation of the sample JS-1. It was collected from a coal seam entrapped in a neovolcanic andesite body of Miocene age. Extreme temperatures, which undoubtedly accompanied the emplacement of this andesite, did not convert local coal into graphite, but only to semianthracite, which can be explained by a relatively short time span and too low pressures to allow for its better recrystallization. Moreover, the δ^{13}C-value did not deviate considerably from that of the original coal.

Carbon modifications

The carbon modifications in the samples under study range from lignite (L), semianthracite (SA), anthracite (A) and metaanthracite (MA) through semigraphite (SG) to a well-ordered graphite (G)(see abbreviations in Table 1), with the following ranges of interlayer distances (in Å): L, SA, A > 3.40, MA 3.38-3.40, SG 3.37-3.38 and G 3.354-3.37. Their structural ordering reflects in the majority of cases the degree of metamorphic overprinting that the host rocks have undergone during their metamorphic evolution. The degree of crystalline perfection has been studied using the x-ray and the TEM methods and the results were reported by Molák et al (1986, 1989) and Molák (1990). These were recently supplemented by few STOE powder diffraction analyses.

Geological setting and metamorphism

The majority of the studied domestic samples have been collected from the Central and Inner Western Carpathians (WC), namely from the Tatricum (or the Core Mountain Zone), the Veporicum and the Gemericum Units. Their assignment to a zone, unit or a mountain is listed in Table 1 and their locations are shown in the attached simplified geological sketches (Figs. 3-7). Few samples come from the Jurassic cover, from the Neogene volcanic rocks, or other lithostratigraphic units. No sketches

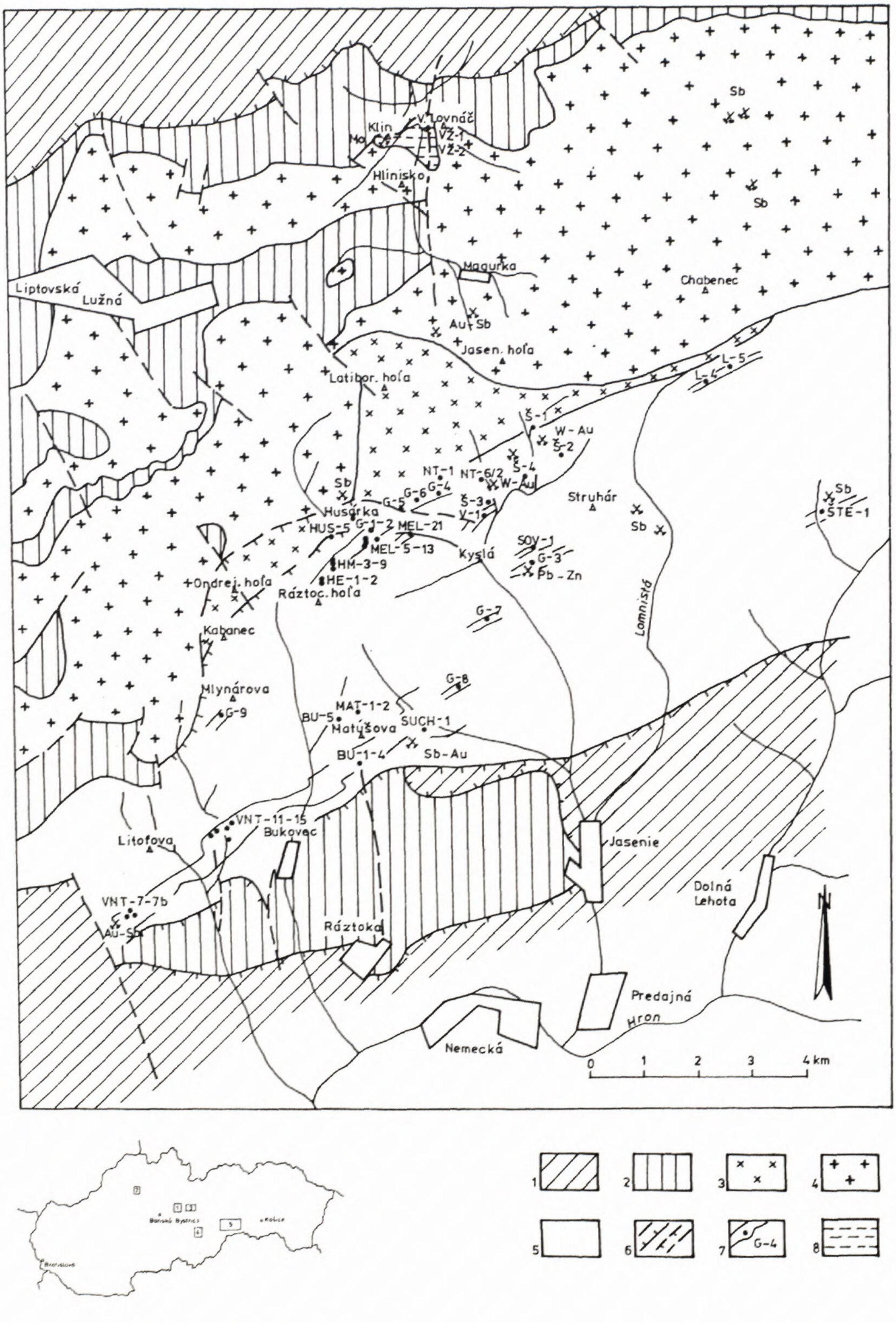


Fig. 3. Schematic geologic map of the central-western part of the Nízke Tatry Mts. (after A.BIELY, O.MIKO, I.LEHOTSKÝ, E. LUKÁČIK, A. KLINEC, B. MOLÁK, J. MICHÁLEK et al.) with sample locations. Legend: 1-Mesozoic nappes; 2-Mesozoic cover; 3-nebulitic migmatite; 4-granitoids; 5.crystalline schists; 6-tectonic lines; 7-layers of SAMP, CFM and graphitic schists; 8-biotitic schist "Klinisko". Crossed hammers: abandoned mines with the main metals extracted.
Inset shows the areas of collected samples: 1-Nízke Tatry Mts., Tatricum Unit; 2-Malá Fatra Mts., Tatricum Unit; 3-Nízke Tatry Mts., Veporicum Unit; 4- souther part of Veporicum Unit; 5-southern part of Gemericum Unit.

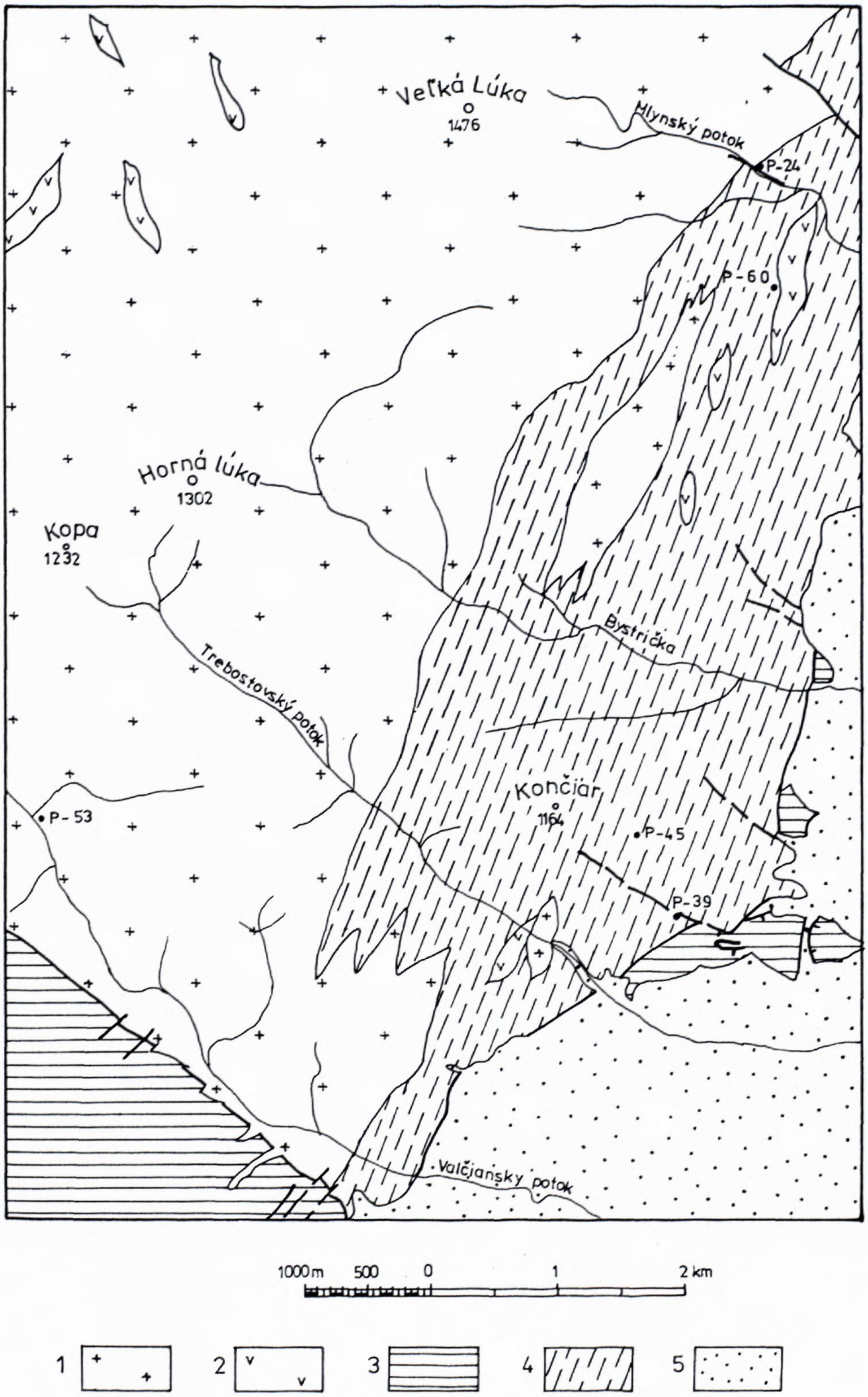


Fig.4: Geologic sketch map of the Lúka part of Malá Fatra Mts.,Tatricum Unit, (after RAKÚS et al. 1993), with sample locations. Legend: 1-Medium grained granodiorite ± pegmatites, aplites (Variscan);2-Amphibolites; 3-Mesozoic carbonate rocks; 4-Garnetiferous biotitic paragneisses ± amphibolites; 5- Neogene and Quaternary sediments.

are presented to show the location of foreign and solitary samples.

Tatricum Unit

According to our metamorphic reconstruction (MOLÁK et al 1986, 1989, KORIKOVSKY - MOLÁK 1995) the CM in the rocks of Tatricum part of the Nízke Tatry Mts. (Fig.3) have been subjected to: 1) Pre-Variscan ultrametamorphism and granitization, accompanied by graphitization of CM; 2) Variscan metamorphism, observed in two levels - a deeper level, exposed to conditions of biotite subzone to amphibolite facies, characterized by a graphitic ± semigraphitic variety of the CM and a shallower level, corresponding to the conditions of chlorite-ankerite-muscovite subfacies, or more precisely, to a depth of burial of 12-13 km, with temperatures of 320-330 °C and pressures of at least 3.5 kbar. The CM has been transformed into anthracite; 3) Alpine anchi- to epizonal metamorphism, accompanied by coalification and anthracitization of the CM. Apart from siderite-ankerite-bearing metasediments, no carbonates occur in the crystalline rocks of the Nízke Tatry Mts. Both Variscan and Alpine stages were characterized by shearing deformations and mylonitization, the former with prevailing ductile and the latter with mostly brittle conditions. Shearing deformations, especially those, of the Variscan stage, were accompanied by migration of mineralized fluids. These were responsible for subsequent development of local Sb, Au, W, base metal and Fe mineralizations, as well as for a re-equilibration with the heavy carbon isotope, or a reaction with water.

In the other mountains of the Tatricum Unit - the Malá Fatra and Suchý - Malá Magura Mts., the well ordered graphites occur in the granitoide, gneissic, schistose and phyllonitic rocks (Fig.4). Probably during the Pre-Variscan orogenetic events the crystalline rocks have been here exposed to amphibolite facies metamorphism. As the schists and the phyllonites contain a completely graphitized CM, they are obviously Variscan diaphthorites.

A sample from the Malé Karpaty Mts., collected from a black shale horizon in an Sb-ore mine near Pezinok, markedly differs from the above samples from the Tatricum Unit by its low metamorphism. The CM was here transformed into semianthracite, which indicates the green schist conditions of metamorphism, and supports the view that the black shales here do not represent an autochthonous cover of the granite core. This is at variance with the situation in the majority of WC core mountains and more reminiscent to that in the Gemericum Unit and in the Eastern Alps.

Veporicum Unit

The Veporicum part of the Nízke Tatry Mts. comprises the Paleozoic volcanisedimentary Jánov Grúň Formation, defined by MIKO (1981). It is composed of the CM bearing dark phyllites and black schists (Fig.5), metasandstones, metagreywackes and metavolcanics. These rocks floor the area south of the Čertovica line, which divides this mountain into the Tatricum and the Veporicum parts. No carbonate rocks are involved. The progressive Variscan metamorphism reached the conditions of green schist facies, with temperatures ranging from 350 to 380 °C and pressures from 3.4 to 4 kbar (MIKO and KORIKOVSKY 1994). Local CM has been converted into semigraphite.

The rocks of the southern Veporicum Unit crop out along the NW side of the Lubeník tectonic line, a line of the first order, separating this unit from the Gemericum Unit. These rocks are composed of Lower Paleozoic metasediments, Variscan and Alpine granitoids and Late Paleozoic sedimentary and volcaniclastic rocks. The studied SG bearing gneisses and schists belong to the Klenovec and Ostrá Complexes - the lowest of the three major stratigraphic and structural horizons (Fig. 6). The reconstruction of Variscan metamorphism has always been hampered by overwhelming presence of Alpine metamorphism and deformational features, by re-orientation of the older structures and by complete resetting of the K/Ar clock. However, the petrologic, structural and fluid inclusion studies indicate that it was characterized by conditions reaching at least the level of biotite isograde, by local emplacements of leucocratic granitoids and by intense shearing. These events markedly affected the southern Veporicum rocks and are considered to have been a consequence of microcontinental collision and obduction of the mobile Paleo-tethian microplate (represented by the Gemericum Unit) over the Alpine-Carpathian microplate, represented by the Veporicum Unit. Shearing deformations were initially compressional, however, progressive erosion of the overthrusted unit resulted in an isostatic uplift of the subducted and geophysically lighter unit, changing the sense of the deformation to extensional. The peak regional metamorphic conditions operated under medium- to high pressures, reaching 6-8 kbars and temperatures exceeding 400 °C (VRÁNA 1964, MAZZOLI et al. 1992). These events were locally overprinted by a contact metamorphism, characterized by zoning of contact minerals within the contact aureole of the Alpine granite intrusions. VOZÁROVÁ (in VÁCLAV et al.1990 inferred) the metamorphic temperatures of 560 °C and the pressures of 2 kbar. CM has been converted into metaanthracite and/or semigraphite.

Gemericum Unit

The Gemericum Unit is composed of Early and Late Paleozoic volcanisedimentary rocks overlain by the Mesozoic Meliata Unit and the Silicicum nappe. This unit comprises prolific deposits and occurrences of polymetallic, Sb, Au, Ag, Hg and Fe ores and sparry magnesite, all mined or explored in the past, but only few mines kept in operation until present day. These mineralizations are frequently located within, or in the vicinity of ubiquitous black shales and lydites, which yielded some of the sam-

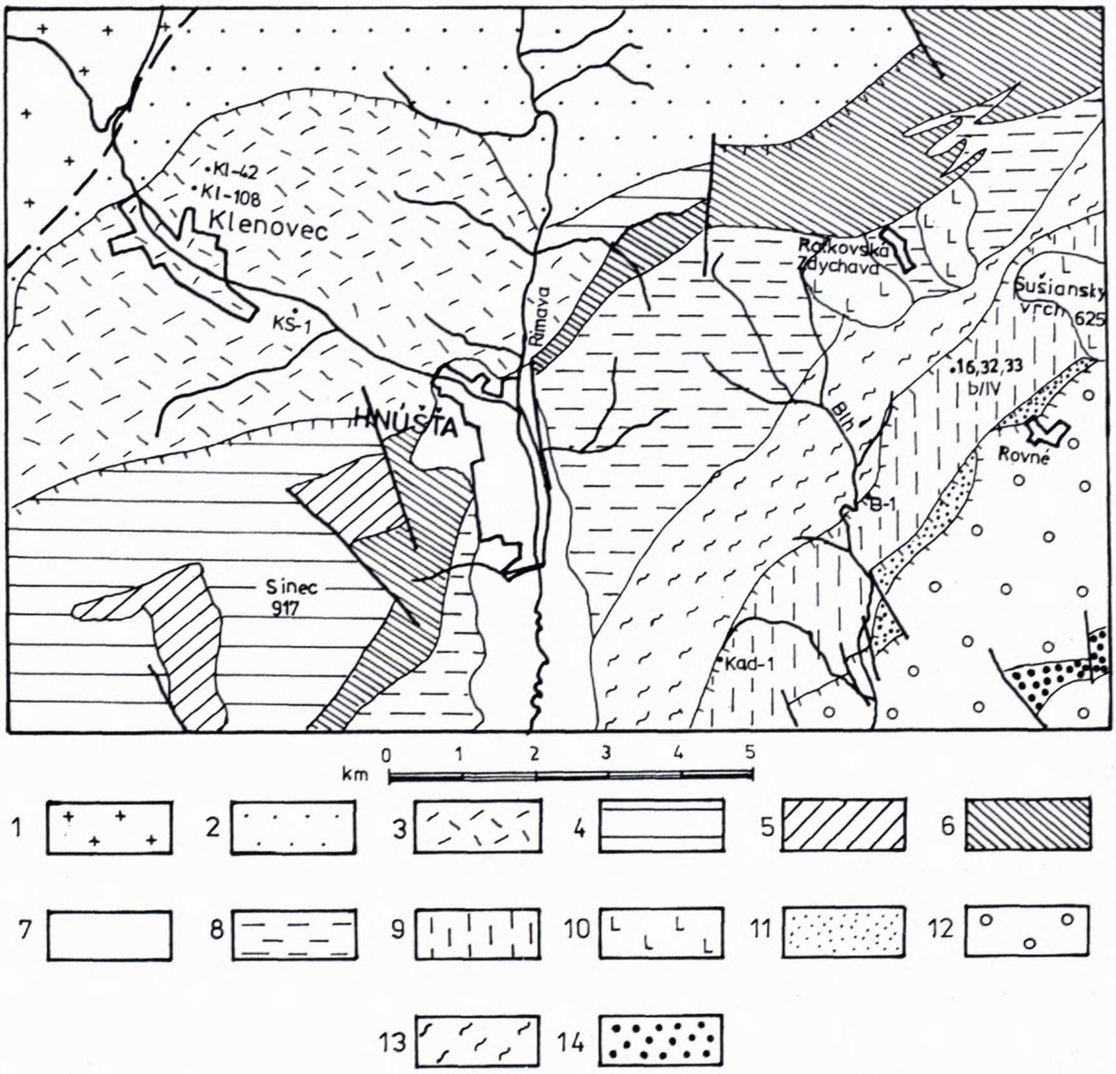


Fig. 5: Geologic sketch map of SW part of the Veporicum Unit (after SLAVKAY et al. 1995), with sample locations. Legend: 1-Hybrid granitoids with transitions to migmatites, locally porphyric (Variscan) 2-Garnetiferous schists, the Ostrá Complex (Paleozoic); 3-Biotitic albitized gneisses, the Klenovec Complex (Paleozoic); 4-White mica-chloritic schists, the Sinec Complex (Paleozoic); 5-Biotitic phyllites, the Hladomorná dolina Complex (Paleozoic); 6- Leucocratic granitoids, the Rimavica Complex (Variscan); 7-Quaternary and Neogene sediments; 8-Dark grey shales, sandstones, phyllites, the Slatvina Formation (Stefanian); 9- Sanstones, shales, basic volcanics, metamorphosed limestones, dolomites, magnesites and ankerites, the Ochtiná Formation, (Late Carboniferous); 10-Volcanics, andesites with pyroclastics(Miocene); 11-Metamorphosed carbonates with basalts, Meliata Group (Triassic-Jurassic); 12-Sandstones, shales, quartzites argillitic limestones, rhyolites, andesites, pyroclastics, the Turnaicum and Silicicum Units (Middle Triassic-Jurassic); 13- Greywackes,shales,volcaniclastics, the Rimava Formation (Permian); 14-Limestones, dolomites, the Turnaicum and Silicicum Units (Middle Triassic-Jurassic).

ples for this isotopic study (Fig. 7). Sedimentary carbonates are represented by limestones of the Carboniferous Zlatník Formation and the hydrothermal carbonates by magnesites, siderites and ankerites. According to b_0 values, measured in white micas by SASSI and VOZÁROVÁ (1987, 1992), the peak regional Variscan metamorphism was characterized by the temperatures ranging from 350 to 430 °C and the pressures between 2 and 2.5 kbar. The range of geothermal gradient has been inferred to have ranged from 40 to 45 °C/km. The Alpine regional tectono-metamorphic processes were marked by shearing deformations and by occassional formation of muscovite. Meanwhile, in the Ochtiná Formation - in the horizon hosting all economic deposits of the sparry magnesite - recrystallization of quartz and formation of radial chloritoide and kyanite, oriented oblique to Variscan mineral association, had taken place locally. No contact effects have been observed in the exocontact of the Alpine granite intrusion and the CM has been here converted into metaanthracite.

Meliaticum Unit

Two CM samples, collected from the drill hole DRŽ-1, which intersected the black shale horizons, were analysed. Black shales belong to the Jurassic Meliaticum Unit, exposed to diagenetic and/or anchizonal conditions during the Alpine metamorphic stage. The CM occurs in anthracitic form.

Methods

All isotopic analyses were performed on demineralized graphitic, subgraphitic or coaly materials The demineralization has been made by flotation and subsequent dilution of the residue in hot concentrated HF and HCl. The synthetic fluoro- or chloro-silicates have been removed by powdered

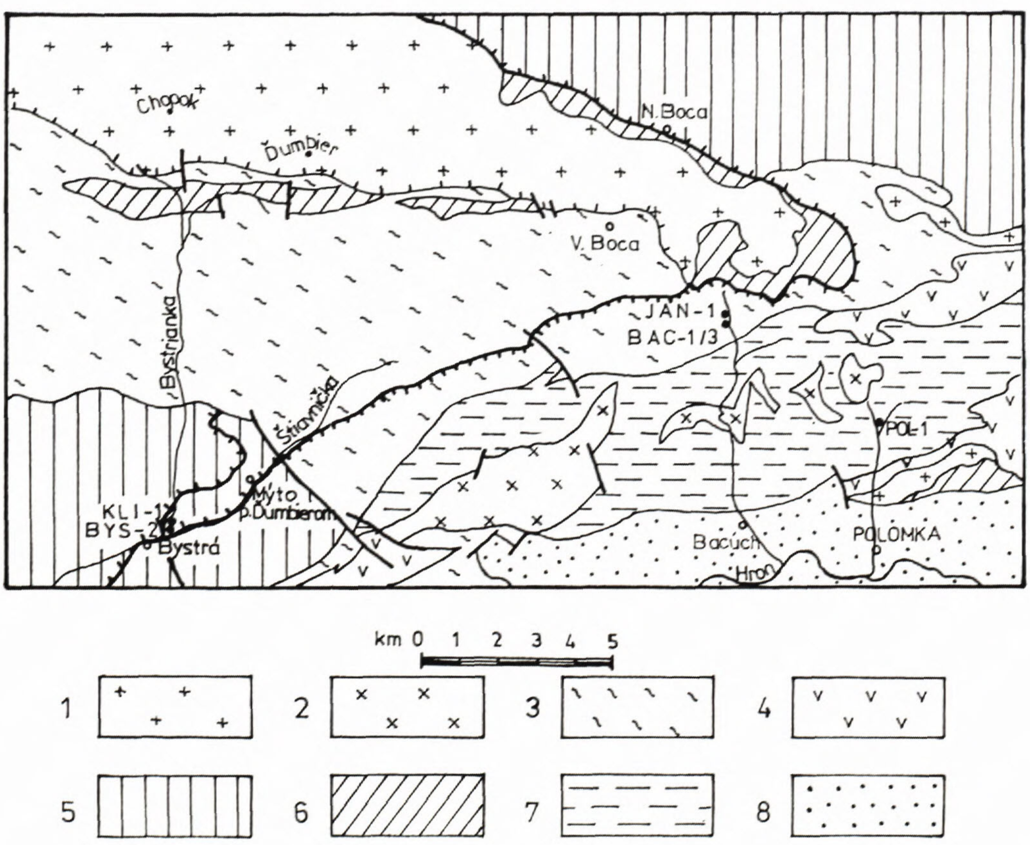


Fig. 6: Geologic sketch map of the Veporicum Unit, Nízke Tatry Mts. (after BIELY et al. 1992) with sample locations. Legend: 1-Granite, granodiorite (Variscan); 2-Granite porphyries and porphyrites (Variscan); 3-Orthogneisses, migmatites (Paleozoic-Pre-Cambrian?); 4-Amphibolites (Variscan); 5-Mesozoic rocks; 6-Triassic quartzites; 7-Paragneisses, schists, phyllites (Paleozoic); 8-Tertiary sediments

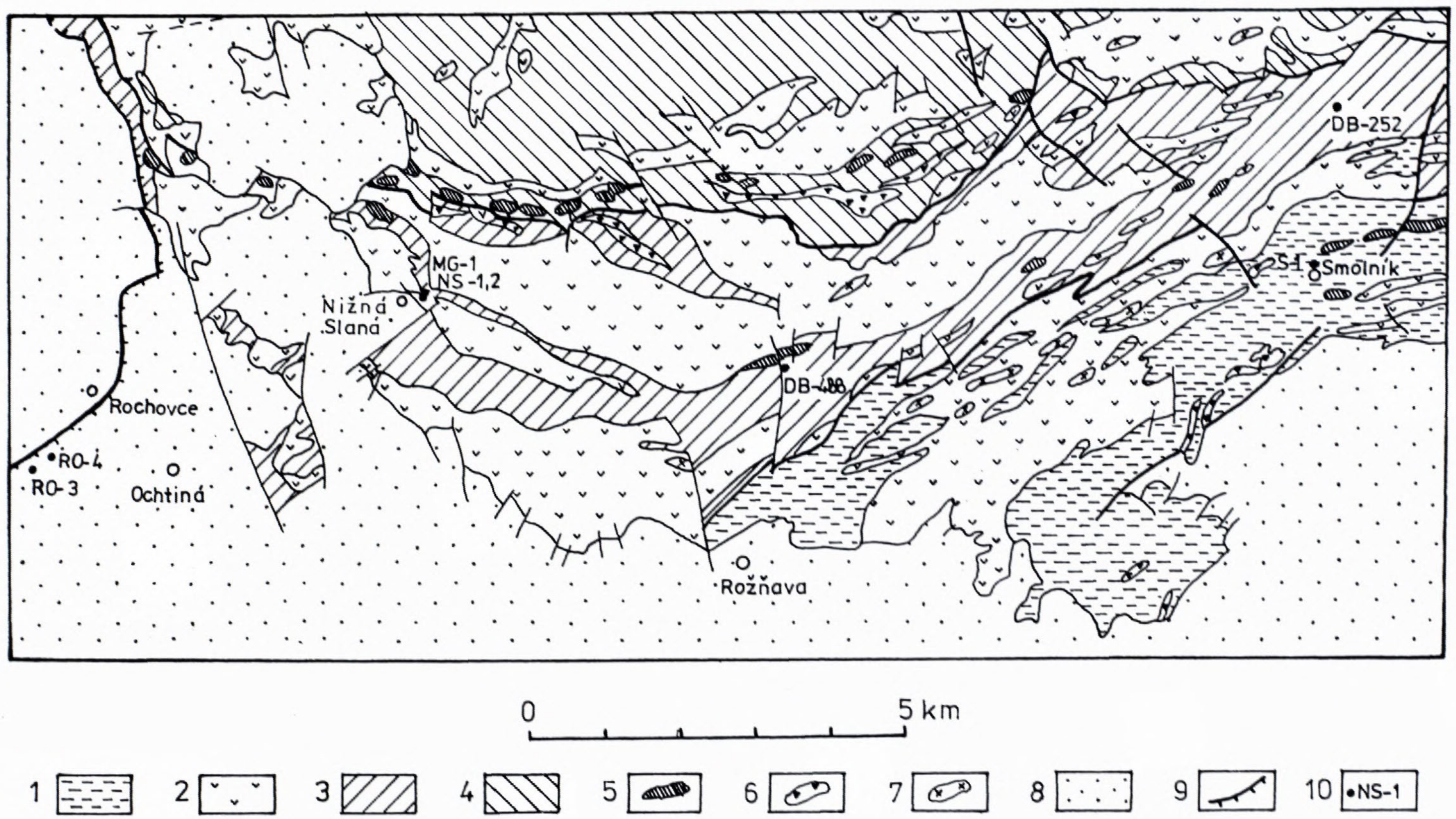


Fig.7: Geologic sketch map of the southern part of Gemericum Unit (after SNOPKO 1974), with sample locations. Legend: 1-Clastic sediments, Upper Silurian-Middle Devonian; 2-metarhyolite tuffs and tuffites, Lower to Middle Silurian; 3-Shales and sandstones, Middle to Upper Silurian; 4- Shales and sandstones, Upper Cambrian to Lower Siluian; 5-Carbonates; 6-Lydites; 7-Quartz porphyries and keratophyres; 8-Late Paleozoic and younger units ; 9-Zone of contact between the Gemericum and Veporicum Units (Lubeník line); 10-sample location

zinc and HCl and by multiple rinsing in hot distilled water. The concentration of carbon in the residues, measured by elemental analysis, was found to vary greatly from few per cent up to 99 per cent, depending mostly on the amount of CM in the host rock and the presence of resistant minerals, pyrite being the most common. The carbon samples were measured for $^{13}C/^{12}C$ composition using a Varian MAT 250 tripple collector mass-spectrometer, installed at the Department of Geology, University of Copenhagen. Analytical results were corrected for mass 46 contributions and recalculated to $\delta^{13}C$ values. The results are reported as per mil deviations from the PDB standard. The reproducibility measured as standard deviation on 10 standard preparations is better than 0.03 per mil on the δ-scale.

Discussion of isotope results

Tatricum Unit, Nízke Tatry Mts.

Most of the investigated carbon samples (40) came from Paleozoic carbonaceous units (CU) of the Nizke Tatry Mts., which crop out in the metamorphic terranes of the Tatricum or Veporicum Units. Among the five groups of CU, defined by MOLÁK et al. (1993), four were measured for isotopes on graphites. These are: 1. nebulites, 2. graphitic schists with Sb-Au mineralization, 3. problematics (metasediments?), and 4. schists of the "Klinisko" type. Furthermore, graphite also occurs in a newly defined lithotype: siderite-ankerite-micaceous phyllite (SAMP), described recently by Korikovsky and MOLÁK (1995). No measurements were made as yet on graphites found in the remaining fifth group, represented by phyllite of the Paučina Lehota type. Locations of samples submitted to isotopic study are shown, together with other samples containing graphitic and/or subgraphitic carbon, in Fig. 3.

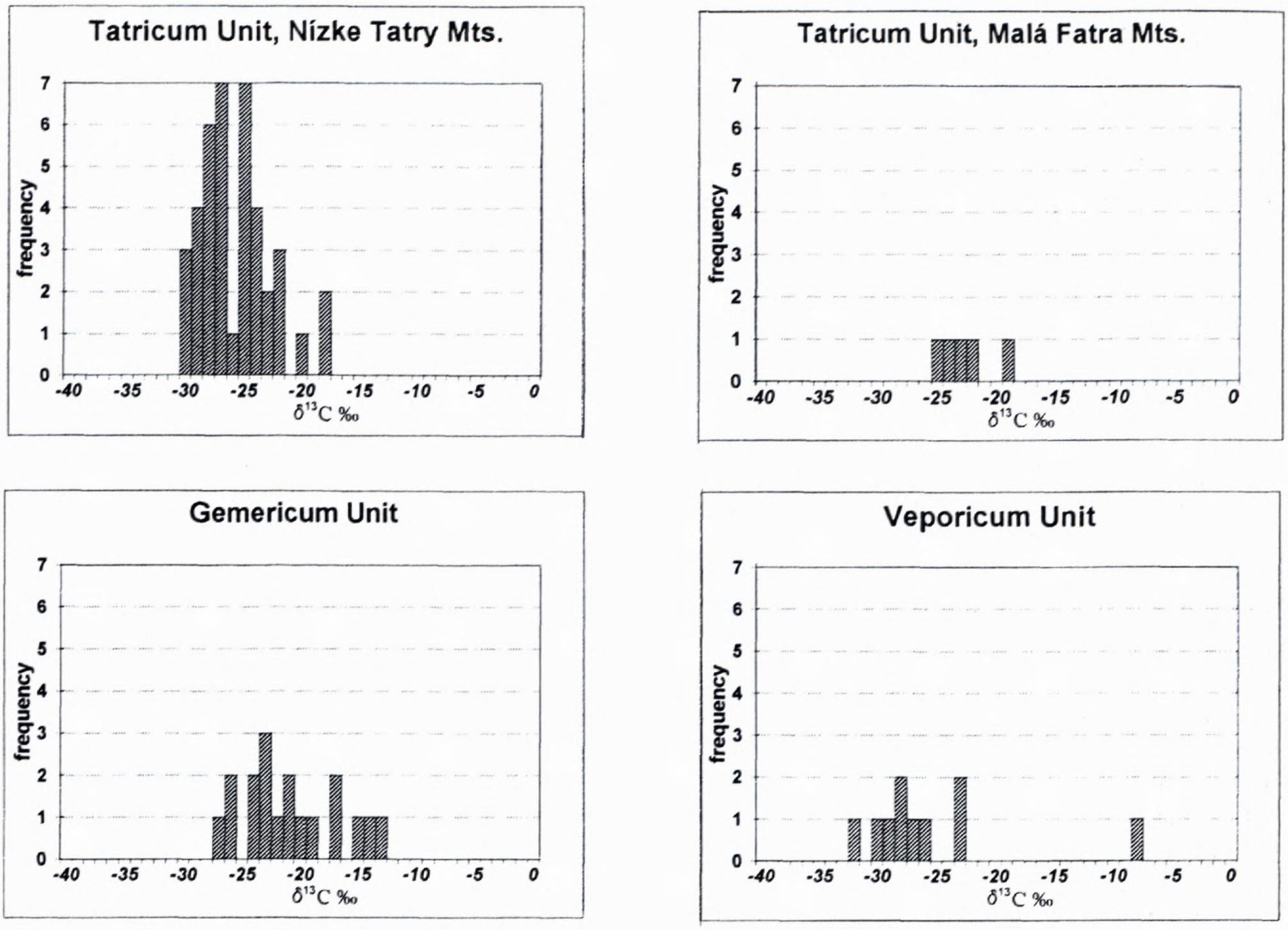
The frequency diagram (Fig.8a) for the samples from the Nízke Tatry Mts. shows that the majority of the $\delta^{13}C$-values range between -30‰ and -22‰. This confirms that (1) the carbon in the samples has an organic source and (2) that none, or only negligible re-equilibration with carbonate carbon took place after its deposition. The occurrence of slightly depleted carbon in some samples ($\delta^{13}C$ -values less than -30‰) may indicate an isotopically lighter precursor, possibly of carbohydrate nature, involved in formation of these CU. However, several black shales of Lower Paleozoic age have been reported to show similar strong depletion in ^{13}C (GALIMOV 1980, BUCHARDT et al. 1986, SCHIDLOWSKI 1986) and the ^{13}C-depleted composition of the Nízke Tatry samples can thus be consistent with suggested Early Paleozoic age of these rocks (MOLÁK et al. 1986 and 1989).

Relative enrichment in the heavy isotope ($\delta^{13}C$ - values around -20‰ or more) has been observed in some of the carbonate-free samples from the above mentioned groups 2 and 3, collected from the zones affected by hydrothermal alteration and shearing, and for some siderite-ankerite metasandstone and phyllite (SAMP) samples. However, the same carbonate minerals as in the SAMP, although in subordinate amounts, may also be present in the group 2 and 3 lithotypes, suggesting a degree of re-equilibration in these rocks as well.

The reported contents of Mg/Fe ± Ca carbonates in the SAMP of the Nízke Tatry Mts. are ~ 4 to 15 wt.% (rarely 40 wt.%) and the average content of graphitic carbon is 0.6 wt.%. Estimated metamorphic temperatures of the host rock did not exceed 300 °C (KORIKOVSKY-MOLÁK, 1995). As expected, the intensity of re-equilibration in a series of SAMP samples shows a linear relation with the carbonate content (Table 1). The progressive shift of $\delta^{13}C$ to more positive values should, in this case, be a function of carbon isotope exchange with the isotopically heavy CO_2, released from the carbonates during metamorphic decarbonation reactions. Decarbonation may commence in the lower greenschist facies and increases with increasing metamorphic grade (SCHIDLOWSKI, in JOHNS 1986). On the other hand, ^{13}C enrichment in the carbonate-free samples, collected from zones of hydrothermal alteration and shearing, should either be related to re-equilibration reactions with the heavy carbon in hydrothermal fluids, or to reactions with water to form ^{12}C enriched CO, thus leaving the remaining graphite relatively enriched in the heavy isotope ^{13}C. A mechanism, similar to the latter case, has been described by ANDREAE (1974) from the Arendal area of Norway. Our structural observations have shown that the propagation of important shear zones with migration of fluids occurred during the Variscan tectono-thermal activity.

Tatricum Unit, Malá Fatra Mts.

PULEC (1992) described graphite disseminated in the granitoids and crystalline schists in the Lúčna part of the Malá Fatra Mts. (Fig. 4). The $\delta^{13}C$-values (Fig. 8b) from 5 samples from this area indicate an organic precursor. Compared to the carbon isotope values from the Nízke Tatry Mts., these values are slightly enriched in ^{13}C. This shift is, in our opinion, associated with the effects of granitization and/or intense metamorphism, which caused a certain

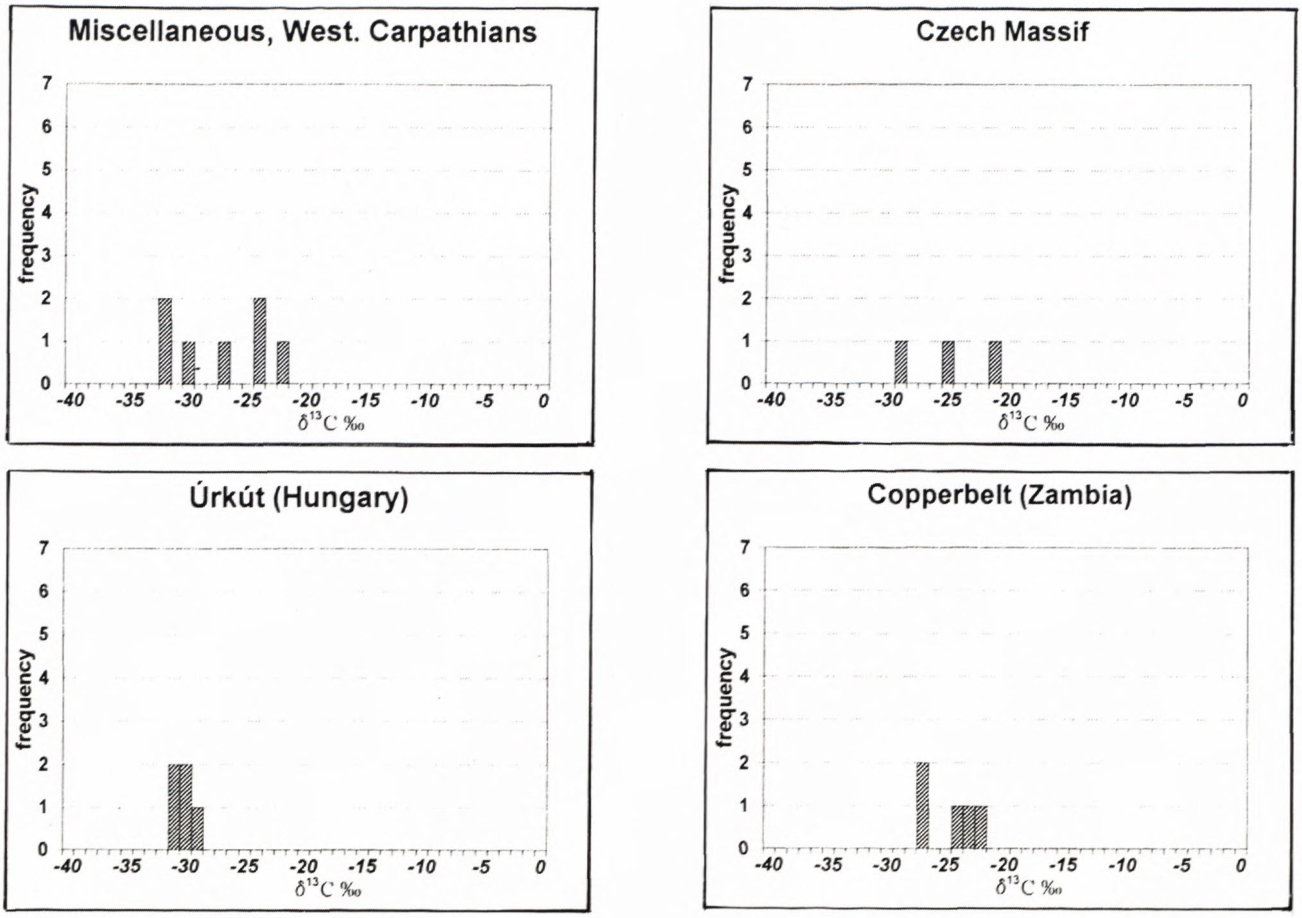


Figs. 8 a,b,c,d and 9 a,b,c,d: Histograms showing the results of isotope analyses.

degree of re-equilibration with juvenile gaseous carbon phase, perhaps in a CO_2 form. The degree of crystalline perfection of graphite is consistent with a deeper structural provenance of these graphite-bearing rocks. Although, this statement should be taken with caution as the number of evaluated samples is too small to allow for a more reliable explanation.

Veporicum Unit

The Veporicum Unit samples from both, the Jánov Grúň Complex and from the Early Paleozoic Klenovec and Ostrá Complexes have been included in a single diagram. The range of δ^{13}C-values for the samples from the Veporicum Unit (Fig. 8c) does not differ significantly from that of the Tatricum samples (Fig. 8a, b). Consequently, the isotope composition of the precursor CM in both units should have been similar, although superimposed metamorphic processes would have been less intense in the Tatricum Unit. A single value that does not match the rest of the data (-8.66 ‰) originates from the southern Veporicum Klenovec Complex. It is a semigraphite found dispersed in a biotitic-albitic paragneiss. This rock was intersected by the borehole KS-1, east of the Klenovec village and the sample was collected from the depth of 154.6 m. This heavily ^{13}C enriched value was first considered to indicate an excessive equilibration with a "juvenile" carbon, or CO_2 with a carbonate precursor. However, the host rock contains neither carbonate, nor any signs of fluid passage, as indicated by the absence of tectonic disruption and alteration zones. The origin of this heavy carbon remains therefore enigmatic, although an alternative explanation could be considered that it was formed in a process of carbonate or carbon dioxide reduction. Similar mechanism has been described by SALOTTI et al. (1971). As a corollary to this observation we note that another semigraphite collected from the same drill hole and the same rock type from a depth of 237.5 m is depleted in heavy carbon (-30.99‰) despite the fact that it originates from a silicified and



Samples in Fig. 9 a: N-2 (3447 m) - Carboniferous anthracitic coal from the basement of the Paleogene flyscht; 52/75 and NEVIDZ- 1- Suchý and Malá Magura Mts.; DRŽ-1 drill hole, depths 90.5 m and 700.4 m; AUG-1 - Augustín adit, Malé Karpaty Mts.; JŠ-1 - coal trapped in an andesite sill.

chloritized zone and an enrichment in the heavy isotope should be therefore more likely.

Gemericum Unit

Comparing the results obtained for samples from the Gemericum Unit with those from the Tatricum and the Veporicum Units a shift towards less negative values can be noted (Fig. 8d). This shift is even more surprising considering the fact that the latter two units evolved within the deeper crustal levels, and having been exposed to more intense metamorphism, they should be enriched in the heavy isotope. However, the anthracite samples from the so called "Magnesite" Carboniferous (Ochtiná Formation) have yielded even more positive $\delta^{13}C$ values and represent, in fact, the most positive values from the entire set. Since the rock metamorphism of this unit is generally low, it could not contribute considerably to the equilibration with coexisting carbonates. Therefore, observed enrichment in ^{13}C should be attributed to either a different organic pedigree or to a different diagenetic pathway of the studied carbon. In other words, the difference in the isotopic composition of reduced carbon in the Gemericum rocks supports the view that the paleoenvironmental development of this unit has been exceptional in respect to other megablocks of the WC system.

Meliaticum Unit

The precursor of anthracite in the studied samples was organic matter. Since the carbonate bearing sample, collected from a shallower horizon, contains isotopically lighter carbon, compared to the carbonate-free sample taken from a deeper horizon (Table 1), no significant re-equilibration with the isotopically heavy carbon can be considered to have occurred here, and the variations in isotope composition can rather be attributed to a higher thermic gradient and more intense pyrolitic reactions than to the influence of carbonate carbon.

Foreign reference samples

Úrkút (Hungary)

Genetic aspects and stable carbon isotope composition of both, the ore-rich and the ore-poor, carbonates from the stratiform sedimentary manganese carbonate ore deposit of Úrkút, Hungary, has been discussed by POLGÁRI et al. (1991, 1992). The results have shown a negative linear correlation with the Mn contents and a negative exponential trend with the total organic carbon content. The authors argue that this mineralization was formed as a consequence of bacterially mediated diagenetic reactions that involved Mn reduction via one or two coupled reactions: the oxidation of organic matter with Mn oxyhydroxide reduction, or the oxidation of FeS produced as a byproduct of seawater sulfate reduction with Mn oxyhydroxide reduction.

Since no isotopic data for organic matter from Úrkút were available, we have analysed 5 samples (Table 1). Our results fall within the range of data for the Tethyan Lower Jurassic, reported by JENKYNS and CLAYTON (1986), but exhibit a more ^{13}C-depleted composition than the average found by these two authors (see Fig.9c).

Based on the present analytical results and previous data the following conclusion can be drawn :

- The Úrkút kerogen, depleted in the heavy carbon isotope, is likely of a bacterial (methanogenic?) derivation.
- Such light carbon could have been partially incorporated into the Mn-carbonates during diagenetic, bacterially mediated, mineralization processes.
- The Mn-richest ores are the most depleted in organic carbon, supporting an assumption that local organic matter has been involved in the mineralization processes.

Copperbelt, (Zambia)

SWEENEY et al. (1986) have undertaken stable isotope studies on sulfides and carbonates from the Konkola area. They observed a strong correlation between concentrations of copper and carbonate carbon. Dolomites from the Ore Shale exhibit $\delta^{13}C$ values ranging from -8.77 to -20.52 ‰ PDB, compatible with a partially organic source for the carbon. In contrast, dolomites from the footwall rocks are notably enriched in ^{13}C (-4.42 to -9.37 ‰ PDB), indicating an influence of marine-derived carbon. Neither in Sweeney's paper, nor elsewhere, were the stable isotope data for organic carbon reported. Altogether 5 samples of OC from various deposits were analysed in this study (Table 1, Fig. 9d).The observed isotopic ratios as well as the average $\delta^{13}C$ value are consistent with organic derivation of carbon, but a degree of equilibration with carbonate carbon is probable. This process was possibly based on the exchange with a gaseous phase, formed as a result of metamorphic and/or fluidization processes that also affected the carbonates. Such processes have obviously taken place simultaneously with the propagation of shear zones, as described recently by MOLÁK (1995) for several of the Copperbelt deposits, particularly those located within the Ore Shale Alignment. The inferred conditions of metamorphism (MOINE et al. 1986) should have corresponded to temperatures of 420 to 550 °C and pressures of 2 to 6.5 kbar. Such conditions are supported also by measurements of graphite crystallinity, with interlayer distances ranging from 3.36 to 3.37 Å. And this suggests the green schist to lowest part of the amphibolite facies metamorphism. The least negative values were found in two of the three measured Mufulira samples, which can be explained by their being exposed to the lowest degree of tectono-thermal effects. However, the third sample is at odds with this postulate. More data are required for further discussion.

Conclusions

Western Carpathians

A review of our isotopic data (Table 1) indicates that the majority of graphites or graphitoids in sedimentary and metamorphic rocks from the Western Carpathians are depleted in the heavy carbon isotope and presumably had sedimentary organic matter as a progenitor. However, some display a shift to ^{13}C enrichment that may have either resulted from a reaction with water, or from re-equilibration reactions with the heavy carbon isotope, both imported to the system in magmatic, metamorphic or hydrothermal fluids. One extremely ^{13}C enriched sample could have formed via reduction of carbonate or carbon dioxide.

The differences in $\delta^{13}C$ values between the Tatricum and Veporicum Units are only minor, consistent with the low degree of metamorphism of their host rocks and suggesting a limited degree of re-equilibration events. The intensity of re-equilibration in carbonate bearing rocks, which were exposed to identical metamorphic conditions, seems to be controlled by relative amount of carbonates in the host rock.

Slightly heavier carbon in the samples from the Gemericum Unit (Table 2) may indicate somewhat different sedimentary/diagenetic conditions and/or a different type of original OM. The latter case would be compatible with a presumption that this unit evolved under different paleoenvironmental conditions, compared to the other major units of the WC system.

Table 2 Average $\delta^{13}C$ values for reduced carbons

Unit/sample Mountain	$\delta^{13}C$ ‰	n
Tatricum Unit - (Nízke Tatry Mts,)	-26.21	40
(Malá Fatra Mts.)	-23.02	5
(Suchý & Malá Magura Mts.)	-32.57	2
Gemericum Unit	-25.25	7
"Magnesite" Carboniferous	-15.59	5
N. Gemericum (Rochovce)	-21.57	5
Veporicum Unit	-27.91	9
Meliaticum Unit (?)	-26.15	2
Foreign samples:		
Zambia		
Copperbelt (Precambrian)	-25.13	5
Hungary		
Mn shales Úrkút (Toarcian)	-30.73	5

The fact that several samples collected from the Tatricum and Veporicum Units contain unusually light carbon suggests to the presence of a very light organic precursor on one hand and to the absence of any re-equilibration, on the other. The most negative values ($\delta^{13}C$ less than -32 ‰) have been found in the samples from the Suchý and Malá Magura Mts. (Table 1, Fig. 9d) as well as in a sample from the Veporicum part of the Nízke Tatry Mts. Their original $\delta^{13}C$-values should have been around -35 ‰, but due to the pyrolitic reactions they should have lost some of their light carbon isotope and became relatively heavier. In general, such extremely negative values are known to occur in Precambrian graphites of bacterial or algal provenance (SCHIDLOWSKI 1986) and this may have been the case also for our samples. While the Precambrian rocks have not yet been documented in the WC, several datings of resistant minerals in metamorphic rocks indicate an import of Precambrian material. Despite its softness, graphite is also a resistent mineral in the geological environment and can be envisaged as a carrier of paleoenvironmetal and/or biological record. We therefore propose that several graphites and subgraphitic matter in Paleozoic sediments or metasediments could have been resedimented from an earlier Precambrian (or older Lower Paleozoic) metamorphic precursor.

Foreign reference examples

Úrkút

The mechanism of bacterially mediated large scale involvement of the OM in the mineralization process and formation of the Mn ores at Úrkút merits further study. Our limited findings support the generally accepted models of Mn mineralization.

Zambian Copperbelt

Our isotopic results support the presumed existence of re-equilibration processes brougt about by the isotopic exchange reactions with the heavy "juvenile" carbon, or with the remobilized carbon derived from carbonate host rocks. These processes were probably associated with the Pan-African metamorphic and tectono-deformational stages that were superimposed on the Copperbelt orebodies. Although the synsedimentary, syndiagenetic model for the Copperbelt orebodies is still applicable in view of many geologists (e.g. FLEISCHER et al. 1976, UNRUG, 1988, GARLICK, 1989), recent observation of shearing structures within the Ore Shale Alignment and the Domes Region as well as the chemical and mineralogical evidence for a broad presence of mineralized fluids in the shearing systems support the epigenetic aspects in the formation of Cu/Co deposits. This finding could be of importance for potential traditional and nontraditional types of Cu/Co mineralization in the Zambian Copperbelt and in the surrounding regions.

Acknowledgements

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