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"BÜNDNERSCHIEFER" METASEDIMENTS OF THE POZDIŠOVCE-IŇAČOVCE UNIT: METAMORPHIC PETROLOGY DATA

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Abstract: The work deals with metamorphic petrology of the rock complexes forming the Pozdišovce-Iňačovce Unit. They are thick complexes of metasediments intercalated by stratiform metaultramafic intrusions and layers of metavolcanic rocks, the "Bündnerschiefer" lithology of which indicates that they belong to the Penninicum. In the phyllitic rocks the determination of metamorphic conditions was based on the study of mineral assemblages. They can be divided into two groups: non-diagnostic: Mu + Pa + Qz ± Ch ± Ab ± Om, stable under very low as well as low-grade metamorphic conditions; diagnostic: Mu + Pa + Py + Qz, Ch + Ctd + Qz. Diagnostic, and mineral assemblages indicate that greenschist facies conditions were reached. The assumed maximal temperatures were between 300 - 400 °C (depending on the composition of coexisting fluid phase). The mineral assemblage Ctd + Py is characteristic for the low to medium pressure range of the lower greenschist facies (Winkler 1979).

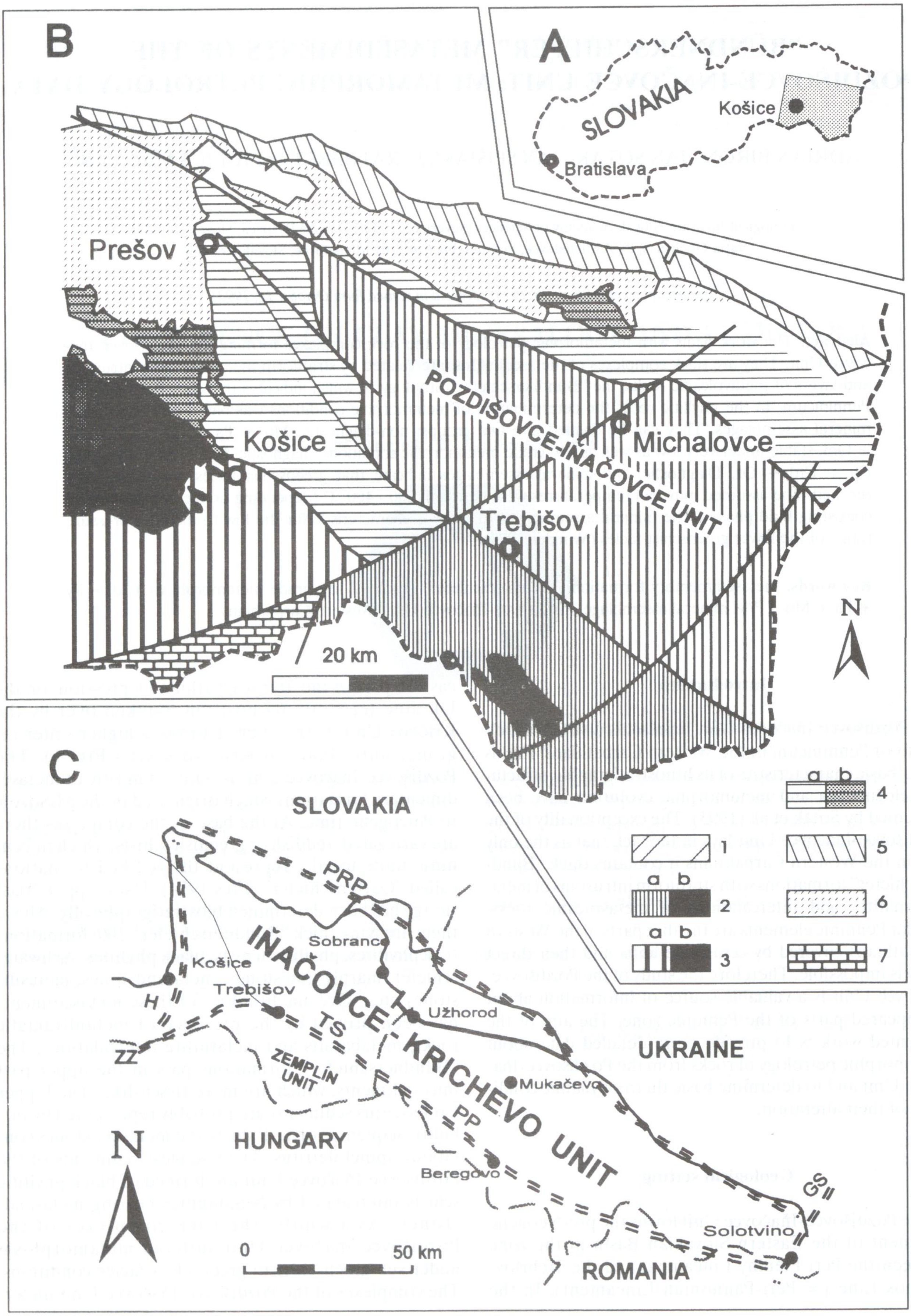
Key words: metasedimentary formation, "Bündnerschiefer" lithology, low-grade metamorphism, Ctd + Py + Pa + Mu +P/M mineral assemblage, Pozdišovce-Iňačovce Unit, Western Carpathians.

Introduction

The Pozdišovce-Iňačovce Unit represents a structural element of Penninicum in the Western Carpathians. In this sense, basic characteristics of its lithostratigraphic, structural-deformation and metamorphic evolution have been presented by Soták et al. (1993). The exceptionality of the Pozdišovce-Iňačovce Unit lays in the fact, that as the only one in the Western Carpahtians it contains thick "Bündnerschiefer" formations with stratiform intrusions of metaultramafites and intercalations of metavolcanic rocks. Similar Penninic elements are in other parts of the Western Carpathians covered by centralide units and their direct study is impossible. Therefore the study of the Pozdišovce-Iňačovce Unit is a valuable source of information about disappeared parts of the Penninic zone. The aim of the presented work is to provide more detailed data about metamorphic petrology of rocks from the Pozdišovce-Iňačovce Unit and to determine basic thermodynamic conditions of their alteration.

Geological setting

The Pozdišovce-Iňačovce Unit forms the pre-Neogene basement of the Eastern Slovakian Basin in the zone between the Peri-Pieniny Lineament and the Trebišov-Szamos Line (= Peri-Pannonian Lineament). In the eastern part of the Transcarpathian Depression, on the Ukraine territory, its position is taken over by the Kričevo Unit, with which it forms a higher-order regional unit (Inačovo-Kričevo Unit - Fig. 1). The Pozdišovce-Iňačovce Unit is built up mostly of metasedimentary formations which originated in the Mesozoic to Paleogene time. At the base of the complexes there are variegated, reddish or greenish schists, which in Penninic units usually represent the red-bed formations called "Qartenschiefer" (Frey 1974). Their Upper Triassic age has been determined biostratigraphically. Above them are lying thick "Bündnerschiefer"-like formations (calcphyllites, phyllitic schists, black phyllites - Schwarzschiefer, marbly limestones, metasandstones, metasiltstones etc.). Oceanic lithology of these metasediments has been proved by the presence of metaultramafic rocks, metabasalts and metatuffite intercalations. The "Bündnerschiefer" formations pass in the upper part into sediments, which are more flysch-like. The Upper Cretaceaous sediments are probably represented by turbiditic sequences of dark shists and metasandstones containing spinel detritus. The youngest sediments of the Pozdišovce-Iňačovce Unit are formed of black phyllitic schists intercalated by Nummulites-bearing metasandstones. As a whole, the rock complexes of the Pozdišovce-Iňačovce Unit suffered metamorphism under sub-greenschist to greenschist facies conditions. The complexes of the Pozdišovce-Iňačovce Unit under-


B
A
SLOVAKIA
Košice
Bratislava
Prešov
Košice
Michalovce
POZDIŠOVCE-INAČOVCE UNIT
Trebišov
N
20 km
a b
4
1
5
a b
2
6
a b
3
7
C
SLOVAKIA
PRP
Sobrance
IŇAČOVCE-KRICHEVO UNIT
Košice
Trebišov
Užhorod
H
TS
ZZ
ZEMPLÍN UNIT
UKRAINE
Mukačevo
PP
N
HUNGARY
Beregovo
GS
Solotvino
0
50 km
ROMANIA

went intensive processes of compressional, extensional as well as strike-slip tectonics. Their main phases, accompanied by syntectonic low-grade metamorhism, occurred in the complexes of the Pozdišovce-Iňačovce Unit probably only after the Eocene. The Neoalpine metamorphism has so far been considered to be a specific Alpine phenomenon (Tauern crystallization or Lepontine metamorphism), having no equivalent in the Western Carpathians. Uncovering of Penninic sequences in the area of the Eastern Slovakian Basin has been caused by oblique synconvergent extension. By the buoyancy of ductile complexes of the Pozdišovce-Iňačovce Unit in the zone of underplate accretion the destabilized parts of the orogenic wedge were detached and unroofed (Soták & Čverčko in print). Similar kinematic mechanisms also drived the unroofing of the Penninic windows in the Alps (cf. Ratschbacher et al. 1990; Genser & Neubauer 1989; Platt 1986; Wallis et al. 1993 etc.).

Basic lithotypes of metamorphic rocks in complexes of the Pozdišovce-Iňačovce Unit

The complexes of the Pozdišovce-Iňačovce Unit are predominantly formed of metapelite formations. Their greatest thicknesses have been drilled by Iňačovce-3 borehole (approx. 1 300 m) and Bunkovce-1 borehole (approx. 800 m). Metapelites of all lithostratigraphic units of the Pozdišovce-Iňačovce Unit (including Eocene metapelites in the Zbudza-1 borehole) contain paragonite, which is the criterion for the rocks to be classified as phyllites (Pamič et al. 1992). The complexes of the Pozdišovce-Iňačovce Unit thus consist of various types of chlorite-sericite, sericite-quartz and carbonate phyllites (Pl. 1, Figs. 1 - 3).

Phyllites of the Pozdišovce-Iňačovce Unit have silky luster and dark or variegated colours. They contain a high propotion of dark organic substance and pyrite. In black metapelite formations, intercalations of chloritoid schists have been found as well (in Iňačovce-3 and Senné-2 boreholes). They are greenish rocks filled with chloritoid aggregates with radial-fibrous structure (Pl. 2, Figs. 1-2).

Metapelitic formations of the Pozdišovce-Iňačovce Unit are often intercalated by metasandstone and metasiltstone beds. Low-grade metasandstones and metasiltstones (e.g. Eocene ones in the borehole Zbudza-1) have blastopsammitic and blastoaleuritic texture. They are mica-bearing, formed mostly of monogenic quartz detritus. With increasing grade of dynamic recrystallization sandstone textures change into quartzitic ones, characterized by triplet contacts of quartz grains.

In calcareous phyllite formations of the Pozdišovce-Iňačovce Unit there are also beds of marbles and marbly limestones (Pl. 1, Fig. 5). They are predominantly pure crystalline limestones with fine-grained granoblastic texture. From primary textures in marbly limestones have been recognized relics of crinoids, echinoids (Pl. 1, Fig. 4) and sporadically also foraminifers.

Ultrabasic rocks occur also in considerable quantities in the complexes of the Pozdišovce-Iňačovce Unit. They have different alteration grades - from relatively fresh peridotites, through serpentinites with relics of primary minerals, chryzotile-lizardite serpentinites up to chlorite-tremolite-actinolite rocks (Pl. 2, Figs. 5-7).

A component of metamorphic formations of the Pozdišovce-Iňačovce Unit are also bodies of metabasalts, pillow breccias and metahyaloclastites.

Metabasalts are amygdaloidal rocks with microblastoophitic texture of matrix and phenocrysts of plagioclases and rarely biotite. Metahyaloclastites have fine-grained devitrified and sericitized matrix, enclosing clasts of fresher effuzives. We recorded also beds of schistose metatuffites. Basic metatuffites are formed of Mg-chlorite base, quartz and the products of mafic mineral alteration (abundant grains of titanite, rutile and actinolite). More acid metatuffites are characterized by the presence of porphyroclasts of chess-board albite, quartz and potassium feldspars (Pl. 1, Fig. 6).

Metamorphism of phyllitic rocks

Methods

Identification of minerals

The minerals have been identified by means of optical and X-ray powder diffraction methods.

For X-ray diffraction (XRD) phase analysis of samples were used whole-rock randomly oriented preparations and fine fractions of below 2 μm. The fraction below 2 μm was obtained by sedimentation. Prior to separation itself, the samples were treated using the method described by Šucha et al. (1991). Separated fractions were used for the preparation of oriented samples, by sedimentation of suspension on glass slides. They were analyzed in air-dry state, after saturation with ethylene-glycol (overnight at 60 °C) or, if necessary, after heating (1 hour at 350 °C). For XRD analyses were used the diffractometers: Philips PW 1710 (CuKα) and DRON 2.0 (CuKα).

The d values in text and in Fig. 2 are in Å (10 Å = 1 nm).

Fig. 1. Geological setting of the studied territory. **A** - selected area in the Eastern Slovakia. **B** - basement units of the Eastern Slovakian Basin and units from adjacent areas.

Legend: 1 - Pozdišovce-Iňačovce Unit; 2 - Zemplinikum: a - in the basin basement, b - cropping out in the "Zemplín Island"; 3 - Gemericum: a - in the basin basement, b - cropping out in the Spišsko-Gemerské rudohorie Mts; 4 - Mesozoic cover nappes: a - in the basin basement, b - cropping out in the Čierna hora Mts (W) and Humenské pohorie Mts (NE); 5 - Pieniny Klippen Belt, 6 - Central Carpathian Paleogene. **C** - situational sketch of the Transcarpathian Depression with units participating in the structure of its pre-Neogene basement. H - Hornád fault, ZZ - Zagreb-Zemplín line, TS - Trebišov-Szamos line, PRP - Peri-Pieniny lineament, PP - Peri-Panonian fault, GS - Ganici- Solotvino fault.

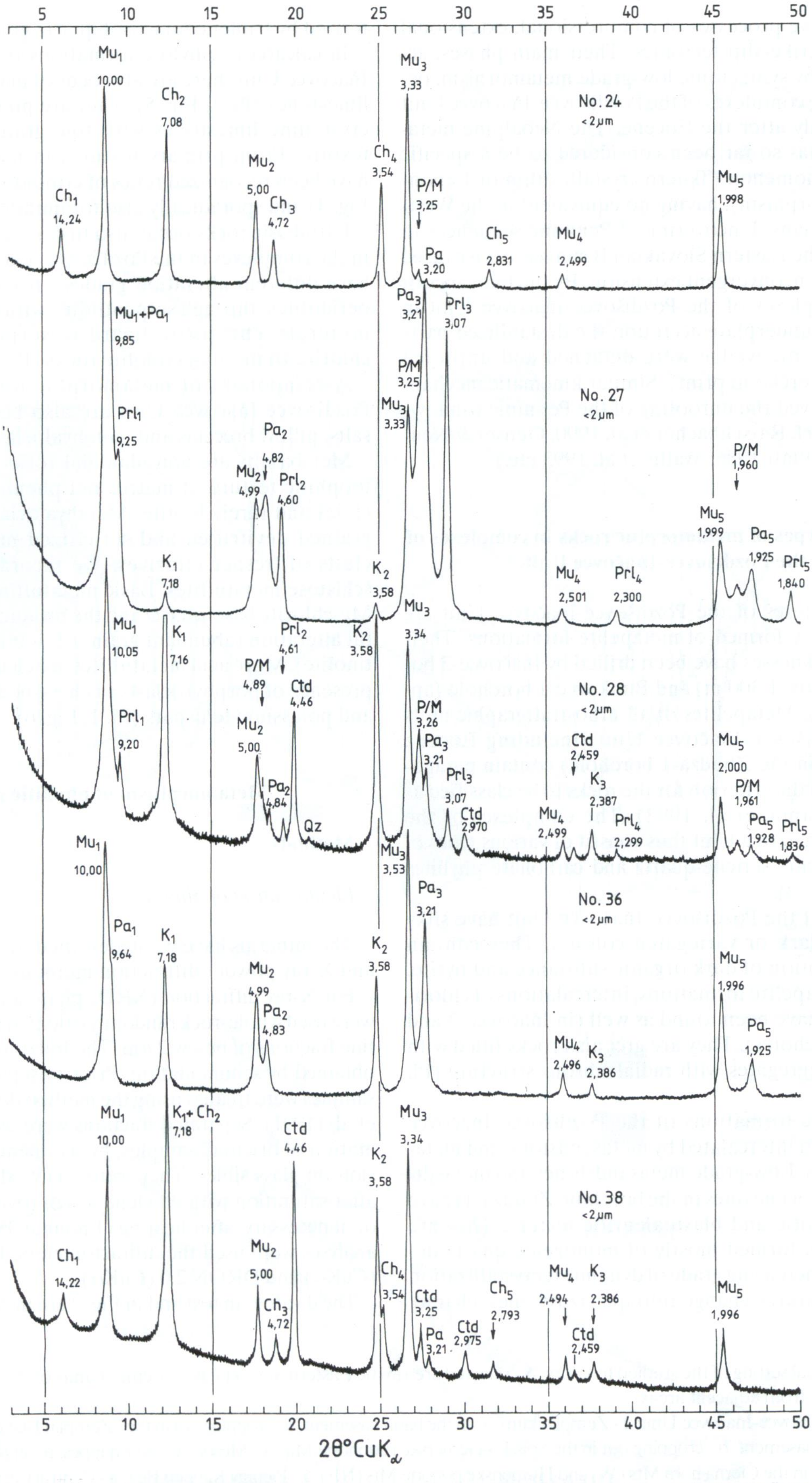


Fig. 2. X-ray diffraction patterns (air dry) of five representative low-grade samples. Mu₁, Mu₂,...Muₙ, refer to the first and subsequent basal reflections of muscovite, etc. (abbrev. see text). Sample locations (No. 24,...) after Tab. 1.

Table 1. Mineral assemblages.

No.	Borehole	m	Rock type	Mu	Ch	P/M	Pa	Prl	K	Qz	Ab	Cc	Do	Om	Others
1	Bun-1	1238-1245	phyllite	x	-	+	+	-	o	+	-	-	-	-	Py,Sid
2	Bun-1	1310-1315	marbly limestone	o	-	+	?	-	+	o	-	x	+	-	
3	Bun-1	1310-1315	marbly limestone	o	-	+	?	-	+	o	-	x	-	-	
4	Bun-1	1429-1434	phyllitic marble	o	+	+	?	-	o	o	-	x	-	-	Py,Sid
5	Bun-1	1429-1434	phylitic limestone	o	+	+	?	-	+	x	-	x	o	-	He
6	Bun-1	1505-1510	calcareous phyllite	o	o	+	o	-	+	o	-	x	-	-	He
7	Bun-1	1597-1602	phyllite	x	x	o	o	-	+	x	-	-	-	-	Tur
8	Bun-1	1597-1602	phyllite	x	o	o	o	-	+	x	-	+	+	-	He,Tur
9	Bun-1	1710-1715	phyllitic marble	o	-	o	o	-	o	o	-	x	-	-	Py
10	Bun-1	1710-1715	phyllitic marble	o	-	o	o	-	o	o	-	x	-	-	Py
11	Bun-1	1930-1935	marble with phyllitic bands	o	-	+	?	-	o	x	-	x	-	-	He,Tur
12	Bun-1	2020-2025	phyllite	x	x	o	o	-	-	o	-	+	-	*	Py
13	Bun-1	2095-2100	phyllite	x	+	+	?	-	+	x	-	-	o	-	Py
14	Zbu-1	2899-2903	phyllite	o	-	+	+	-	+	o	o	x	o	*	I/S,Py
15	Zbu-1	2999-3002	quartz phyllite	x	x	+	+	-	-	x	o	+	o	*	
16	Zbu-1	3118-3122	phyllite	x	x	+	+	-	-	x	o	+	o	*	
17	Zbu-1	3202-3207	bituminous phyllite	o	o	+	+	-	-	x	o	+	o	*	Py
18	Zbu-1	3300-3304	phyllites with metapsammites	x	x	+	+	-	-	o	+	+	-	*	
19	Zbu-1	3511-3514	phyllites with metapsammites	o	o	+	+	-	+	x	o	+	+	*	Py
20	Zbu-1	3594-3597	phyllites with metasiltstones	o	+	+	+	-	o	x	o	-	-	*	
21	Zbu-1	3697-3700	phyllitic metasiltstone	x	x	+	+	-	-	x	o	+	o	*	Py
22	Iňa-3	2166-2171	phyllite	x	x	+	+	-	+	x	+	-	-	-	Py
23	Iňa-3	2215-2220	quartz phyllite	o	x	+	+	-	+	x	o	+	-	*	Py
24	Iňa-3	2305-2308	phyllitic quartzite	x	x	+	?	-	+	x	o	+	-	-	Py
25	Iňa-3	2865-2870	calcareous phyllite	x	x	+	+	-	+	x	+	+	o	-	Py
26	Iňa-3	3000-3004.5	phyllite	x	-	o	x	x	+	+	-	-	-	-	Sid
27	Iňa-3	3000-3004.5	phyllite	x	-	o	x	x	o	+	-	-	-	-	Sid
28	Iňa-3	3000-3004.5	oritoid schist			o	o	+	o	x	-	-	-	-	Ctd(X).Lcx,Sid
29	Iňa-3	3110-3115	phyllite (metatuffite)	o	o	+	+	-	+	x	+	+	-	-	
30	Iňa-3	3110-3115	phyllite (metatuffite)	x	x	+	?	-	+	+	-	+	+	-	
31	Iňa-3	3181-3183	black phyllite		x	o	o	-	+	x	+	+	-	*	Ctd(+)Py
32	Iňa-3	3349-3354	black phyllite	x	x	o	o	-	-	x	-	o	-	*	Py
33	Iňa-3	3496-3500	black phyllite	x	o	o	o	-	-	+		x	+	*	Ctd(O)Py
34	Poz-1	2100-2103	quartz phyllite	x	-	o	x	-	o	x	-	-	o	-	Py,Sid
35	Poz-1	2100-2103	quartz phyllite	x	-	o	x	-	o	x	-	-	o	-	Py,Sid
36	Poz-1	2100-2103	phyllite	x	-	?	x	-	o	x	-	-	o	-	Py,Sid
37	Poz-1	2181.5	dolomitic phyllite	x	-	o	x	-	+	x	-	-	o	-	Py,Tur,Sid
38	Sen-2	3282-3282.5	chloritoid schist	o	+	-		-	o	x	-	-	-	-	Ctd(X),Sid
39	Reb-1	3678-3681	green schists-metaultramafites	+	x	-	-	-	-	+	x	-	-	-	Ac,Ti,Ru
40	BPol-1	1297-1302	calcareous phyllite	x	x	+	?	-	+	+	+	x	-	*	Py

x - major phase, o - minor phase, + - trace phase, ? - presence questionable, * - presence

Boreholes: Bun-1 = Bunkovce-1, Zbu-1 = Zbudza-1, Iňa-3 = Iňačovce-3, Poz-1 = Pozdišovce-1, Sen-2 = Senné-2, Reb-1 = Rebrín-1, BPol-1 = Blatná Polianka-1

Chemical composition of minerals

Chemical analyses of minerals were carried out on electron microprobe Cameca-Camebax (Dept. of Mineralogy and Petrology, University Padova, Italy) at standard conditions.

Areal distribution of elements and EDX analyses were studied using electron microprobe JEOL JXA/840 A (analyst Ing. J. Lokaj). Relations between selected groups of minerals were studied by SEM, the apparatus JEOL JSM/840 (Dr. J. Stankovič).

Mineral abbreviations:

Ab - albite, Ac - actinolite, Cc - calcite, Ce - celadonite, Ch - chlorite, Ctd - chloritoid, Do - dolomite, He - hematite, I/S - mixed-layer illite/smectite, K - kaolinite, Lcx - leucoxene, Mu - muscovite, Om - organic matter, OPx - orthopyroxene, Pa - paragonite, P/M - mixed-layer paragonite/muscovite, Prl - pyrophyllite, Py - pyrite, Qz - quartz, Ru - rutile, Ti - titanite, Sid - siderite, Tur - tourmaline.

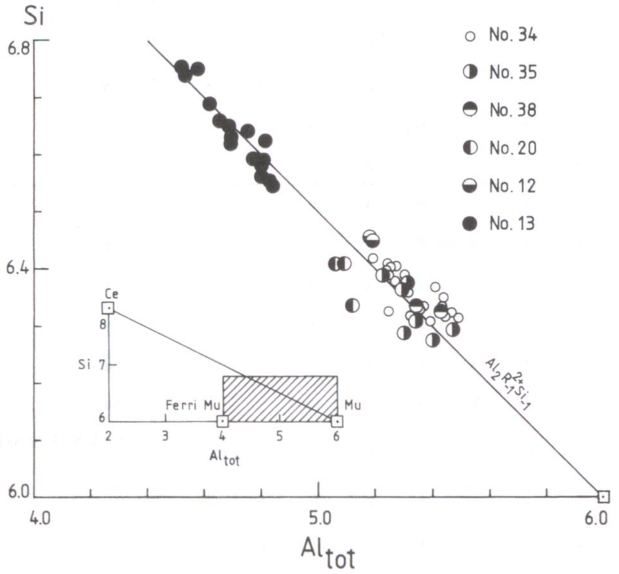


Fig. 3. Microprobe analyses of white K-micas plotted in a Si-Al$_{tot}$ diagram (after Hunziker et al. 1986).
Sample No.13 contains a low alumina assemblage, samples 12, 20, 34, 35 and 38 contain high alumina assemblages. Sample locations (No. 12,...) after Tab. 1.

Table 2. Electron-microprobe analyses of muscovite. Structural formulae are calculated on the basis of 22 oxygens.

No.	12 (n=2)[1]	13 (n=16)	20 (n=3)	34 (n=1)	35 (n=1)	38 (n=2)
SiO_2	48.98	49.79	47.80	47.59	47.46	48.24
TiO_2	0.16	0.14	0.61	0.21	0.12	0.04
Al_2O_3	33.42	29.98	32.49	34.53	32.86	34.82
Cr_2O_3	-	0.03	0.05	-	-	0.14
FeO[2]	1.60	2.70	1.60	2.09	2.74	1.76
MnO	0.03	0.01	0.05	0.05	0.05	0.01
MgO	1.12	2.13	1.53	0.61	0.95	0.90
CaO	0.02	0.01	0.01	0.00	0.17	0.01
Na_2O	0.49	0.25	0.38	0.78	0.96	0.73
K_2O	9.96	10.17	10.36	9.40	8.46	9.17
Anhydrou stotal	95.76	95.21	94.87	95.26	93.77	95.82
Si	6.446	6.639	6.387	6.308	6.388	6.331
Al^{IV}	1.554	1.361	1.613	1.692	1.612	1.670
T. site	8.000	8.000	8.000	8.000	8.000	8.000
Al^{VI}	3.631	3.349	3.503	3.701	3.600	3.715
Ti	0.016	0.014	0.061	0.021	0.012	0.004
Cr	-	0.003	0.005	-	-	0.014
Fe	0.176	0.301	0.179	0.231	0.308	0.194
Mn	0.003	0.002	0.005	0.005	0.005	0.001
Mg	0.220	0.424	0.304	0.120	0.191	0.177
O. site	4.045	4.093	4.058	4.079	4.117	4.105
Ca	0.002	0.002	0.002	0.001	0.025	0.002
Na	0.124	0.064	0.099	0.201	0.251	0.185
K	1.672	1.730	1.766	1.589	1.453	1.536
I. site	1.799	1.796	1.867	1.791	1.728	1.722

[1] = Number of analyses
[2] = Total Fe as FeO
Sample locations (No. 12,...) after Tab. 1.

Mineralogy

The following minerals have been determined in the studied rocks: quartz, muscovite, chlorite, mixed-layer paragonite/muscovite, paragonite, calcite, albite, kaolinite, dolomite, siderite, organic matter, pyrite, hematite, pyrophyllite, chloritoid, tourmaline, actinolite, titanite, rutile, apatite, zircon. In this part we shall mention only those in which chemical composition has been analyzed, or if a detailed description of identification is desirable.

White K-micas. This phase has been found exclusively in the form of $2M_1$ polytype. Chemical composition of white K-micas was studied in several samples. However, due to very fine-grain size, it was difficult to obtain uncontamined analyses. The results are presented in Tab. 2 and Figs. 3, 4 and 5.

Chemical composition of fine-grained matrix muscovites depends on mineral assemblages (Guidotti & Sassi

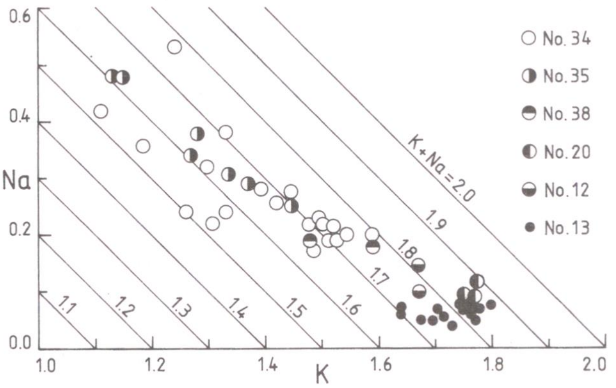


Fig. 4. Microprobe analyses of K-white micas plotted in Na-K diagram.
The linear array of analyses points for samples 34 and 35 is due to the fine intergrowth of muscovite and paragonite. Sample locations (No. 12,...) after Tab. 1.

1976). High-alumina assemblages in samples 12, 20, 34 and 38 (Tab. 1) contain relatively Al-rich muscovites with low contents of celadonite component (Si = 6.33 - 6.45) (Fig. 3). On the other hand, the assemblage with lower Al contents in sample 13 contains muscovites richer in the celadonite component (Si = 6.64). The same relationship can be seen on Fig. 5, where the composition of muscovites from these assemblages is plotted into a muscovite - celadonite - pyrophyllite diagram. The celadonite substitution increases from assemblages with maximal paragonite contents (samples 34 and 35) to the assemblage where the presence of paragonite is uncertain (sample 13, see below). Points of analyses in the Si - Al_{tot} diagram (Fig. 3) are located parallelly with the Tschermak exchange vector $Al_2R^{2+}{}_{-1}Si_{-1}$ (muscovite-celadonite solid solution line). Thus, the contents of Fe^{3+} (ferrimuscovite component) is negligible (Hunziker et al. 1986; Frey et al. 1988).

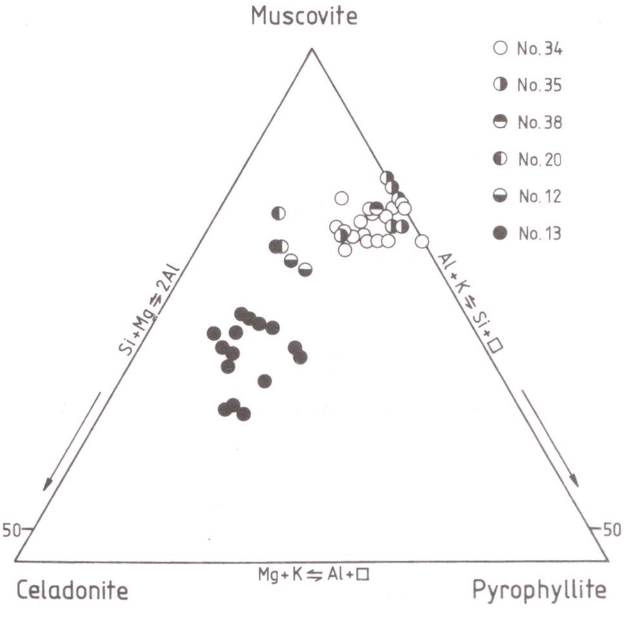


Fig. 5. Composition of muscovite expressed in terms of muscovite ($K_2Al_6Si_6O_{20}(OH)_4$), pyrophyllite ($Al_4Si_8O_{20}(OH)_4$), and celadonite $K_2Mg_2Al_2Si_8O_{20}(OH)_4$) end-member components (after Hower & Mowatt 1966).
See text for discussion. Sample locations (No. 12,...) after Tab. 1.

Microprobe analyses of white K-micas in samples with maximal paragonite contents (Tab. 1, samples 34 and 35) are affected by the presence of this mineral. The relationship of paragonite *vs.* muscovite has been studied by means of distribution Na and K, as well as the BSE study of thin sections. In paragonite-muscovite aggregates, a more or less homogeneous distribution of Na has been recorded. This fact is caused probably by very fine intergrowths of these two mineral phases (Fig. 6). This is confirmed also by the very wide range of chemical composition of these white micas, especially as far as interlayer cations are concerned (Fig. 4). Therefore, a microprobe analysis of pure paragonite could not be obtained from any of the 27 analyses points. Maximal Na content was 0.53 atoms per formula unit (a.f.u.) (Na/Na+K = 0.30). The most representative chemical composition of muscovite could be in this case the analysis with highest K content and maximal occupation of interlayer positions (Frey et al. 1988). The contents of Na are then 0.20 (sample 34) and 0.25 (sample 35) a.f.u. (Na/Na+K = 0.11, or 0.15; Tab. 2). The Na contents in assemblages with lower quantities of paragonite (samples 12, 20 and 38; Tab. 2) vary in the range of 0.09 - 0.19 a.f.u. (Na/Na + K = 0.05 - 0.12) and in sample 13, where the presence of paragonite is uncertain (see below), in the range of 0.04 - 0.08 a.f.u. (Na/Na+K = 0.02 - 0.04). Except in samples 34 and 35 these values are low and they are consistent with low-temperature formation of muscovites. Ca contents are negligible.

The occupation of interlayer positions in the studied samples never attains the ideal value of 2 a.f.u.. The highest values have been determined in sample 20, where (K+Na) = 1.87 and greatest vacancies in muscovites from samples 34 and 35 (K+Na = 1.67 and 1.66), which could be caused also by lower quality of microprobe analyses (see above). Lower occupation of interlayer positions in muscovites of lower greenschist facies is however in no way unusual (see e.g. Stephens et al. 1979; Franceschelli et al. 1991).

In sample 13 it was possible to compare the composition of fine-grained matrix muscovites with the composition of relatively larger muscovite flakes, probably of detritic origin. At the same time, the zoning of coarse-grained muscovites was investigated. However, as it can be seen on Figs. 3 and 4, their composition is almost identical. Such reequilibration of chemical composition between muscovites of detritic and authigenic origin is possible only in metamorphic conditions of greenschist facies and it is an evidence of chemical equilibrium state (Hunziker et al. 1986).

Paragonite. Paragonite was indentified by XRD analysis of oriented preparations based on first three basal reflections (Fig. 2). It was distinguished from margarite through the measurements of (00.10) basal reflection

(Frey et al. 1988). However, in several cases is its presence uncertain (Fig. 2, sample 24). Safe identification by means of XRD methods was not possible probably due to very small quantity of this mineral.

Mixed-layer paragonite/muscovite. This mineral was for the first time described by Frey (1969). It was identified by its strong basal reflection at 3.25 Å. If present in greater quantities, further basal reflections at 4.88 Å and 1.96 Å are present too (Fig. 2).

Pyrophyllite. Pyrophyllite was identified on the basis of its first three basal reflections (Fig. 2) and it was distinguished from talc by its (060) reflection. The BSE study of thin sections allowed to determine the presence of large crystal aggregates of pyrophyllite within a fine-grained muscovite-paragonite-pyrophyllite matrix (Fig. 7).

Chlorite. Chlorites forming the matrix of metapelites were too fine-grained for microprobe analyses. However, several samples contain chlorites which form a part of synmetamorphic quartz-calcite veins. They form "annelid"-like aggregates (Pl. 2, Fig. 3) and cause the greenish colour of the quartz. Chemical composition of these chlorites from samples 12 and 24 is listed in Tab. 3. According to nomenclature of Hey (1954), these chlorites belong to ripidolites and plot into the composition field of chlorites from greenschist facies rocks (Fig. 8, after Velde 1977). Fan-shaped chlorite aggregates have been found too, however, they are not a component of metamorphic assemblages, but of the filling of Fe-carbonate veinlets (sample 38; Pl. 2, Fig. 4). Tab. 3 shows for a comparison also the chemical composition of chlorites from basic metatuffites (sample 39). These chlorites have, in comparison with previous ones, lower Al contents, higher Mg contents and they can be classed with pyknochlorites (Hey 1954). Similarly as with white K-micas, the dependence of chlorite composition on the bulk composition of the rocks is here evident as well.

Chloritoid. Chloritoid has been determined in four cases (Tab. 1, samples 28, 31, 33 and 38, Fig. 2). The scarceness of its occurrence in metapelites of appropriate metamorphic grade is caused by a strong dependence of the stability of this mineral from the whole-rock composition. The occurrence of chloritoid is related to rocks with high Al and Fe contents (Hoschek 1969; Winkler 1979). In samples 28 and 38, where chloritoid is dominant, there was on the basis of X-ray criteria of Halferdahl (1961) determined the presence of triclinic structural modification of this mineral. Average chemical composition of chloritoids from samples 28 and 38 is listed in Tab. 3. Structural formulas have been calculated on the basis of 12 oxygen atoms (water-free). The Fe^{2+}/Fe^{3+} ratio has been calculated assuming that the equation $|4 - M^{3+}| = 2. |2 - M^{2+}|$ (M^{2+} without Ca; Chopin et al. 1992) is valid. The values of X_{Fe2+} (Tab. 3) vary in the range of 0.902 - 0.922, or 0.850 - 0.890, and the values of X_{Mg} in the ranges 0.073 - 0.093 or 0.100 - 0.129. The negligible contents of K, Na and Ca indicate that there is no coherent intergrowth with phyllosilicates described by Banfield et al. (1989). The contents of Mn and Fe^{3+} are negligible as well. From above data it is

Table 3. Electron-microprobe analyses of chlorite and chloritoid. Structural formulae are calculated on the basis of 14 oxygens for chlorite and of 12 oxygens for chloritoid.

	chlorite				chloritoid	
No.	12	24	39		28	38
	(n=4)$^+$	(n=4)	(n=9)		(n=6)	(n=12)
SiO_2	23.82	25.53	27.68		24.19	24.07
TiO_2	0.06	0.02	0.04		0.03	0.16
Al_2O_3	21.67	21.79	18.33		39.78	39.34
FeO^*	34.58	26.18	21.85		26.21	25.92
Cr_2O_3	0.02	0.02	0.02		0.01	0.06
MnO	0.19	0.25	0.26		0.15	0.28
MgO	7.77	13.88	19.36		1.35	1.87
CaO	0.02	0.04	0.06		0.01	0.01
Na_2O	0.00	0.01	0.01		0.02	0.02
K_2O	0.01	0.00	0.05		0.01	0.01
Anhydrous total	88.16	87.70	87.66		91.76	91.74
Si	2.631	2.698	2.864	Si	2.032	2.024
Al^{IV}	1.369	1.302	1.136			
Total	4.000	4.000	4.000			
Al^{VI}	1.451	1.412	1.099	Al	3.938	3.898
Ti	0.005	0.002	0.003	Ti	0.002	0.010
				Fe^{3+}	0.035	0.080
Fe	3.194	2.314	1.891	Fe^{2+}	1.807	1.742
Cr	0.001	0.002	0.001	Cr	0.000	0.004
Mn	0.018	0.022	0.023	Mn	0.011	0.020
Mg	1.280	2.187	2.986	Mg	0.169	0.234
Total	5.949	5.938	6.004	Total	5.962	5.989
Ca	0.003	0.004	0.006	Ca	0.001	0.001
Na	0.001	0.001	0.003	Na	0.003	0.003
K	0.002	0.000	0.006	K	0.001	0.001
Total	0.005	0.005	0.015	Total	0.005	0.005
$X_{Fe}^{2+} = Fe^{2+}/(Fe^{2+} + Mn + Mg) =$					0.910	0.873
$X_{Mg} = Mg/(Fe^{2+} + Mn + Mg) =$					0.085	0.117
$X_{Mn} = Mn/(Fe^{2+} + Mn + Mg) =$					0.005	0.010

$^+$ = Number of analyses
* = Total Fe as FeO
Sample locations (No. 12,...) after Tab. 1.

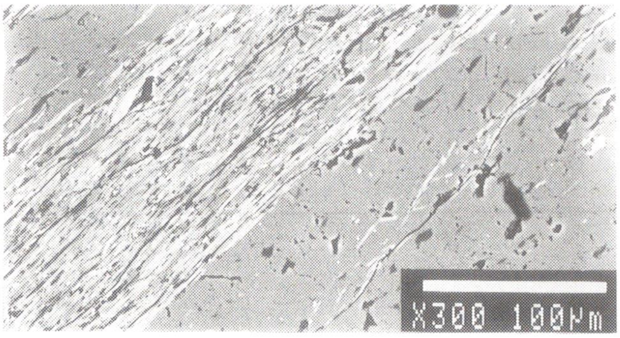


Fig. 6. BSE image of mica strip composed of finely interlayed muscovite and paragonite crystals.
Pozdišovce-1 borehole (2100 - 2103m, sample 35, Tab. 1). Magnif. 300 x.

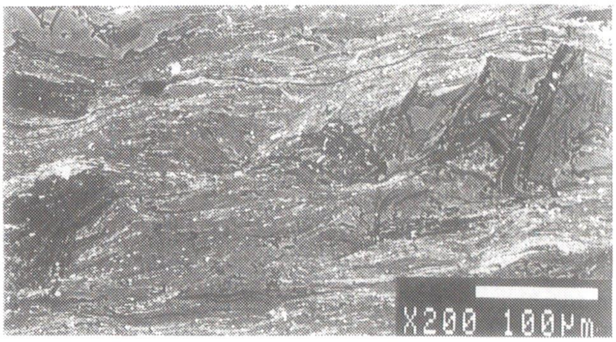


Fig. 7. BSE image of large pyrophyllite crystals (dark-grey) within the fine-grained matrix composed of muscovite- paragonite-pyrophyllite and quartz. White coloured stripes represent Ti-oxide impregnations.
Iňačovce-3 borehole (3000 - 3004.5 m, sample 26, Tab. 1). Magnif. 200x.

evident that it is a chloritoid *sensu stricto*, i.e. Fe-dominant (Chopin et al. 1992)

Plagioclase. From some analyses of plagioclases in samples 20 and 39 it follows that their composition corresponds to pure albites.

Carbonates. Carbonates heve been identified using XRD methods and EDX analyses. We determined the presence of calcite, Fe-dolomite and siderite (Pl. 2, Fig. 4).

Organic matter. As organic matter was considered the black material floating on the surface of water column during the separation of fine fractions. Its characteristics, such as coal rank, C contents etc., have so far not been studied in greater detail.

Secondary minerals. Secondary minerals are represented by kaolinite, mixed-layer illite/smectite and unidentified ore minerals.

Mineral assemblages

Mineral assemblages in 40 samples of low-grade metamorphic rocks of the Pozdišovce-Iňačovce Unit are listed in Tab. 1.

As mentioned above, we assume that chemical equilibrium has been reached in the studied metapelites. In spite of this, inequilibrium mineral assemblages have been found as well. They are above all the assemblage chloritoid + mixed-layer paragonite/muscovite and pyrophyllite + mixed-layer paragonite/muscovite (samples 27, 28, Fig. 2). Mixed-layer paragonite/muscovite is a metastable precursor of paragonite and muscovite (Frey 1987b). Its stability should not exceed metamorphic conditions of the middle anchizone (e.g. Merriman & Roberts 1985; Robinson & Bevins 1986; Korikovsky et al. 1992), where it breaks down into two distinct minerals. The existence of this mineral in metamorphic conditions necessary for the origination of pyrophyllite and chloritoid (see below) is therefore more than improbable. The determined facts are not in accordance with the previously quated data. The authors have no explanation for this.

Chloritoid schists (samples 28 and 38) are also characterized by high contents of kaolinite. It is possible to explain its presence by retrograde processes during postmetamorphic alteration of pyrophyllite, to a lesser extent also chloritoid (Goffe et al. 1987; Jiang et al. 1990).

Mineral assemblages from Tab. 1 represent a multicomponent system SiO_2-Al_2O_3-FeO-Fe_2O_3-MgO-CaO-Na_2O-K_2O-H_2O-CO_2, which can be divided into following subsystems:

Subsystem Na_2O-K_2O-Al_2O_3 *(plus excess* SiO_2-H_2O*)*. The following mineral assemblages have been detemined in this subsystem (AKNa diagram): muscovite, muscovite-paragonite, muscovite-paragonite-pyrophyllite and muscovite-paragonite-albite. It is necessary to stress here, that mixed-layer paragonite/muscovite is present in all types of assemblages. These assemblages represent the pyrophyllite-paragonite-albite facies (Thompson & Thompson 1976).

Subsystem Al_2O_3-MgO-FeO *(plus excess* SiO_2-K_2O-H_2O*)*. This subsystem (diagram AFM) is represented by the assemblages: chlorite, chlorite-chloritoid, pyrophyllite-chloritoid.

Conditions of metamorphism

From the viewpoint of the determination of physical conditions of metamorphism, mineral assemblages occurring in the studied metasediments can be divided into two groups. The first one are so-called non-diagnostic assemblages, including muscovite + paragonite + quartz ± albite ± organic matter and muscovite + chlorite + paragonite + quartz ± albite ± organic matter. These assemblages are predominant (Tab. 1) and are stable under very low-grade as well as low-grade metamorphic conditions (sub-greenschist and greenschist facies) (Frey 1988).

The second group consists of assemblages found only scarcely, allowing however an approximate estimation of especially temperature conditions of metamorphism. They are the assemblages: muscovite-paragonite-pyrophyllite- quartz, chlorite-chloritoid-quartz and chloritoid-pyrophyllite-quartz.

There are several experimental works and thermodynamic calculations dealing with the stability of pyrophyllite. The values for the lower and upper stability limits suggested by various authors are however to a considerable extent different. For example, at the pressure of 3 kbar and $a_{H2O} = 1$ the presence of pyrophyllite indicates a temperature range of 320 - 395 °C (Chaterjee et al. 1984), 315 - 420 °C (Helgeson et al. 1978) or 305 - 395 °C (Berman et al. 1985). What more, the application of such data to concrete mineral assemblages is made even more difficult by the absence of data on the composition of fluid phase. In case that the fluid phase contains CO_2 and CH_4, water activity is reduced and thus the temperature stability field of pyrophyllite becomes slightly wider. The boundary values are shifted towards lower temperatures. In such cases the mentioned temperatures must be considered as the maximum (Frey et al. 1988; Evans & Guggenheim 1988).

Chloritoid was generated most probably according to the reaction:

$$\text{pyrophyllite} + \text{chlorite} \rightarrow \text{chloritoid} + \text{quartz} + H_2O$$

(Zen 1960). According to thermodynamic calculations of Baltatzis (1980), equilibrium of this reaction falls into the temperature interval of 400 - 435 °C ($P_{H2O} = 3$ kbar), depending on the used chlorite model. However, as stressed by Frey et al. (1988), the reaction must take place at a temperature lower than the breakdown point of pyrophyllite. The application of these results becomes again complicated due to the composition of fluid phase.

Pressure conditions of metamorphism have not been yet specified more precisely, mostly because of the fact that the use of the most accessible geoberometer - b_0 parameter of white-K micas - is prevented by the whole-rock composition of the metasediments (see e.g. Guidotti & Sassi 1976). However, the presence of the assemblage chloritoid-pyrophyllite indicates conditions corresponding to the range of lower to medium pressure of the lower greenschist facies (Winkler 1979; Chopin & Schreyer 1983).

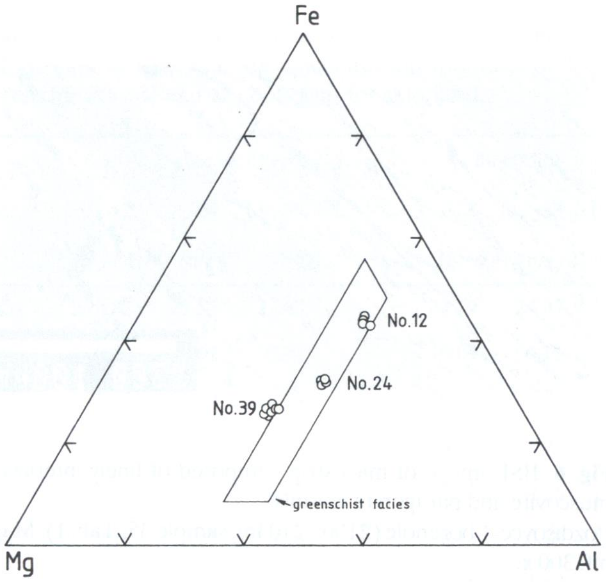


Fig. 8. Al-Fe-Mg diagram showing chemical composition of chlorites. Composition field of chlorites from the greenschist facies after Velde (1977).

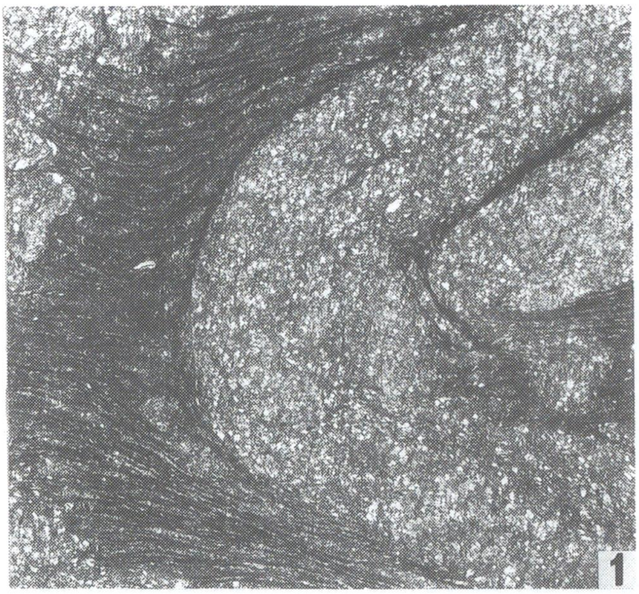
On the basis of the presence of chloritoid it can be thus stated that metamorphism of the rocks of the Pozdišovce-Iňačovce Unit reached the greenschist facies conditions at the maximal temperature probably ranged between 300 - 400 °C.

These conclusions can be supported by a comparison of mineral assemblages from the metasediments with assemblages of metabasaltic rocks. Tab. 1 shows the only representative example, the assemblage chlorite-actinolite-albite-titanite-rutile (sample 39, the study of these rocks has not been finished yet). The absence of prehnite and pumpellyite and abundant presence of actinolite are evidences of reaching the greenschist facies, at which the actinolite is originated at temperatures of about 300 °C (Bird et al. 1984; Cho & Liou 1987).

We attempted to use chlorite geothermometer for a more precise determination of temperature (Cathelineau & Nieva 1985; Cathelineau 1988). This thermometer is based on a positive linear correlation between the contents of Al^{IV} and temperature. Although it has been developed for chlorites from geothermal environment (geothermal system Los Azufres, Mexico), it

Plate 1

Fig. 1 - Folded metasiltstones with penetrative crenulation cleavage in metapelitic bands. Iňačovce-3 borehole (2215 - 2220 m, sample 23, Tab. 1). Magnif. 7.5 x (plane-polarized light). Fig. 2 - Strongly deformed phyllite showing the segmentation to the cleavage - microlithons. Senné-8 borehole (3495 - 3500 m). Magnif. 7.5 x (plane-polarized light). Fig. 3 - Crenulated phyllites from the Zbudza-1 borehole where they are interlayered with nummulite-bearing metasandstones. Depth 3118 - 3122 m. Magnif. 7.5 x (plane-polarized light). Fig. 4 - Echinoid spine in the marbly limestones from the Iňačovce-3 borehole (2667 - 2671m). Magnif. 24.5 x (plane- polarized light). Fig. 5 - Marble with the mica-rich intercalation which is deformed as a kink bands. Blatná Polianka-1 borehole (1297 - 1309, sample 40, Tab. 1). 24.5 x (crossed polars). Fig. 6 - Metatuffite with pre-s_1 generated plagioclase crystaloclasts. Iňačovce-3 borehole (3110 - 3115m, sample 29, Tab. 1). Magnif. 48 x (plane-polarized light).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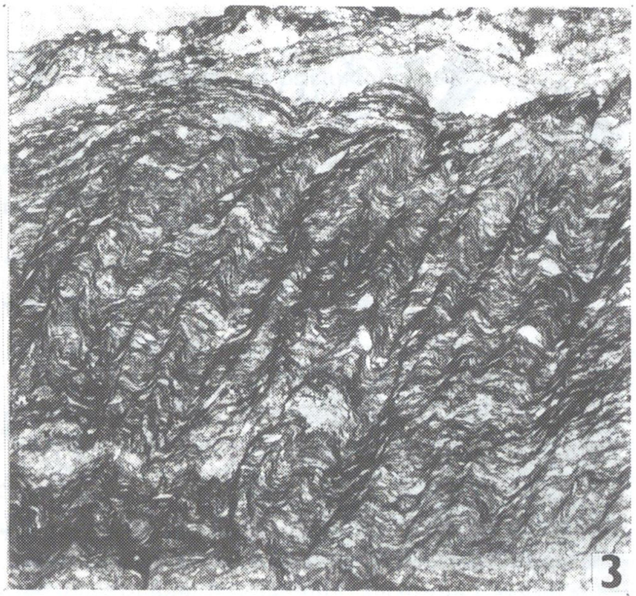
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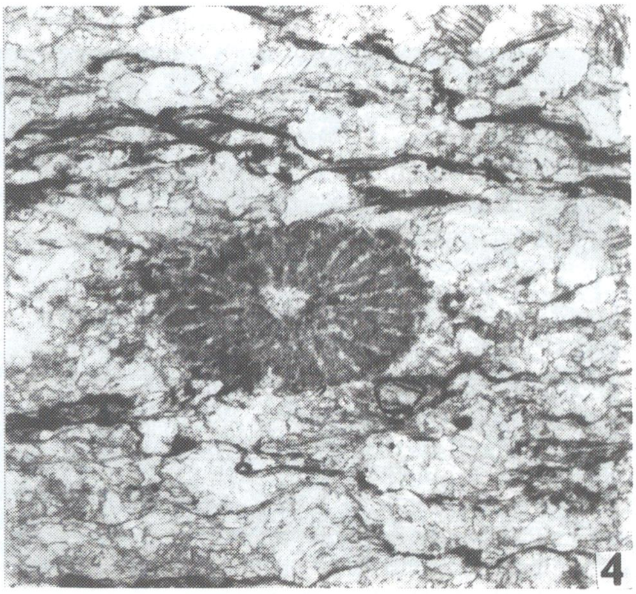
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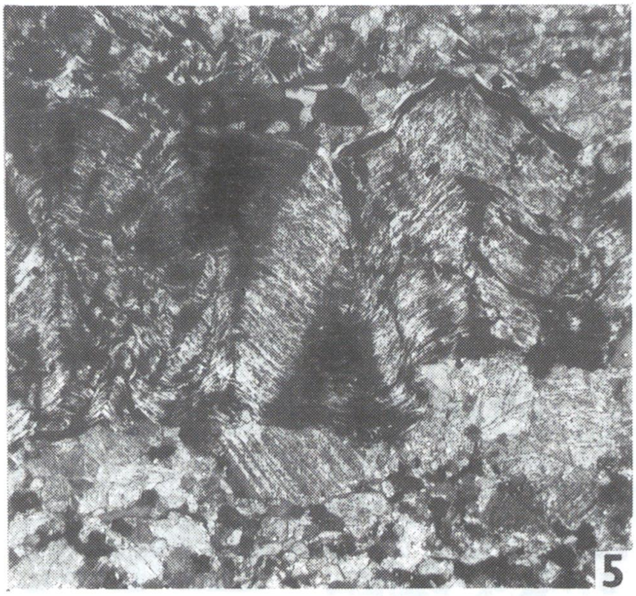
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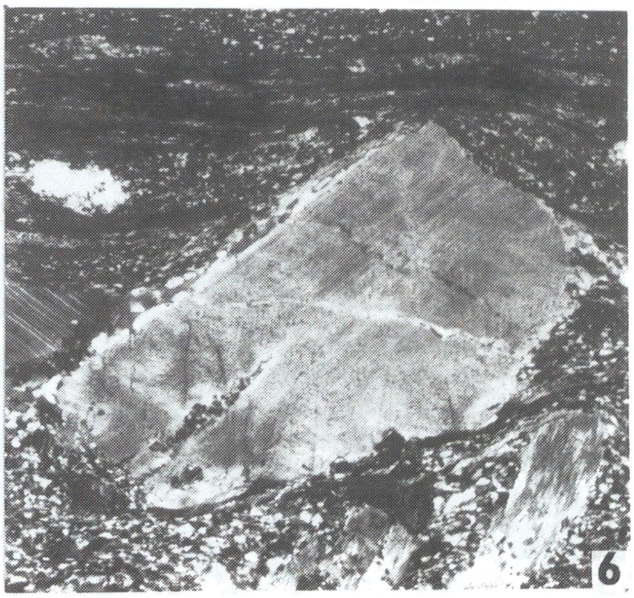
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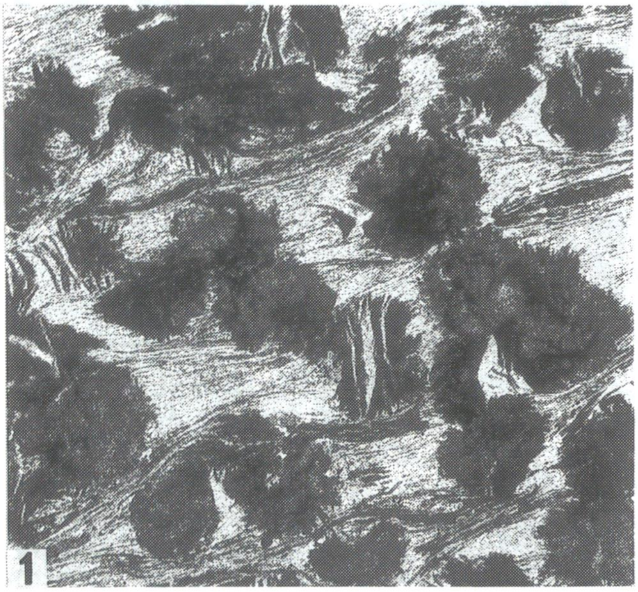
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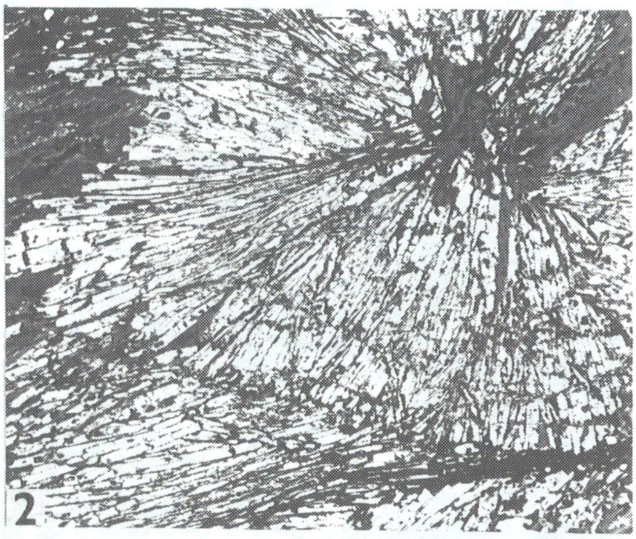
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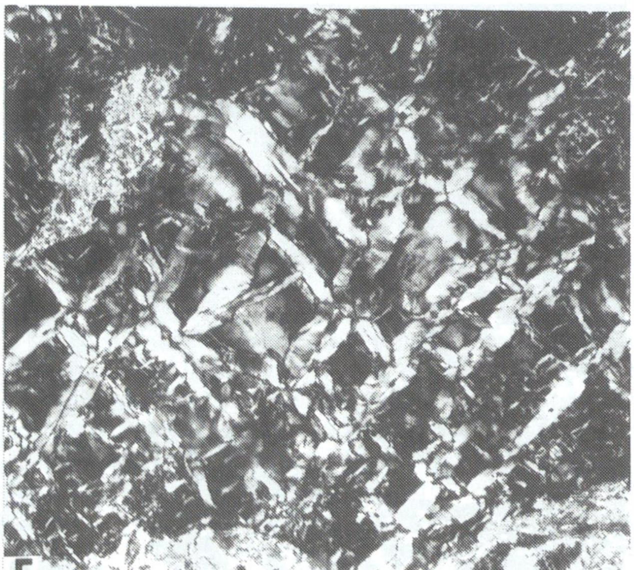
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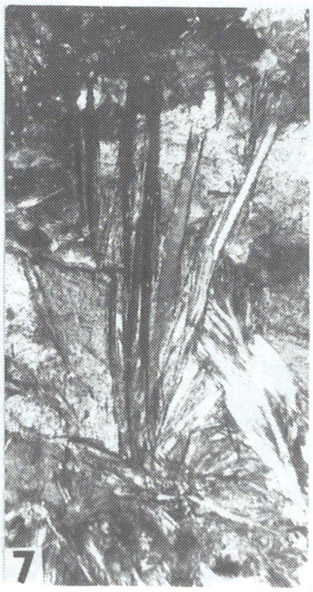
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has been recently successfully applied to mafic phyllosilicates of regional low-grade metabasites (Bevins et al. 1991). Cathelineau (1988) reported that chlorite geothermometer could be probably successfully used also for chlorites of diagenetic, hydrothermal or metamorphic origin, if the contents of Al in tetrahedral positions appears to be independent of the rock lithology or the composition of fluids. For the calculation of temperatures we used chlorites from metabasalts (sample 39) as well as chlorites from synmetamorphic quartz-calcite veinlets (sample 12, and 24). In the first case we determined values of about 304 °C, which is consistent with the average temperature of 309 °C reported by Bevins et al. (1991) for chlorites from greenschist facies metabasites from Wales and eastern North Greenland. In the second case the calculated temperatures are considerably higher, 379 or 357 °C. We consider the results of chlorite geothermometer from metabasalts, but especially from synmetamorphic veinlets to be preliminary and their verification requires a larger set of data.

Conclusions

Complexes of the Pozdišovce-Iňačovce Unit consist of metasedimets of low metamorphic facies. In their mineral assemblages we identified quartz, muscovite, chlorite, mixed-layer paragonite/muscovite, paragonite, calcite, albite, kaolinite, dolomite, siderite, organic matter, pyrite, hematite, pyrophyllite, chloritoid, actinolite, rutile, titanite, apatite, tourmaline and zircon. From the viewpoint of the metamorphic physical conditions the mineral assemblages present in the studied rocks can be divided into two groups. The first group consists of so-called non-diagnostic assemblages, which are predominant. Here belong the following assemblages: muscovite + mixed-layer paragonite/muscovite + paragonite + quartz ± chlorite ± albite ± organic matter. These assemblages are stable under the conditions of very low (in the sence of illite "crystallinity" anchizone), as well as low-grade metamorphism (greenschist facies) (Frey 1988).

The second group consists of assemblages found only in a few cases (Iňačovce-3 and Senné-2 boreholes), which however allow a more accurate estimation of metamorphic temperature conditions. They are the assemblages muscovite + paragonite + pyrophyllite, chlorite + chloritoid and chloritoid + pyrophyllite. Pyrophyllite is a product of kaolonite dehydration occurring at temperatures of 280 - 330 °C (Frey 1987a). Chloritoid formed most probably according to the reaction pyrophyllite + chlorite → chloritoid + quartz + H_2O. Equilibrium of this reaction falls according to thermodynamic calculations of Baltatzis (1980) into the temperature range of 400 - 435 °C. An inevitable precondition for this reaction is however the fact that the temperature must not reach the breakdown point of pyrophyllite, which occurs in the range of 387 - 420 °C (Spear & Cheney, 1989; Berman et al. 1985; Chaterjee et al. 1984).

Pressure conditions of metamorphism have not been specified yet more accurately, due to the fact that whole-rock composition of the metasediments is not favourable for the use of b_0 parameter of white K-micas (see e.g. Guidotti & Sassi 1976). The presence of the assemblage chloritoid + pyrophyllite however indicates conditions corresponding to the range of low to medium pressures of the lower greenschist facies (Winkler 1979; Chopin & Schreyer 1983).

On the basis of above mentioned facts we can assume that maximal attained temperature conditions of metamorphism ranged between 300 - 400 °C, at assumed low or medium pressures. Some variations of metamorphic conditions towards lower temperatures can be neither excluded, nor confirmed, since due to ubiquity of paragonite the method of illite "crystallinity" could not be used. However, the presence of this mineral itself as an distinct phase indicates that conditions of the medium grade of anchizone have been reached (e.g. Merriman & Roberts 1985).

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Plate 2

Fig. 1 - Chloritoid schists with rosette-like chloritoid aggretates which show syngenetic formation with s_1 planes. Senné-2 borehole (3282 - 3282.5 m, sample 38, Tab. 1). Magnif. 12.5 x (plane-polarized light). Fig. 2 - BSE image of chloritoid aggregatest showing the radial-fibrous structure. Iňačovce-3 borehole (3000 - 3004.5 m, sample 28, Tab. 1). Magnif. 190 x. Fig. 3 - "Annelid" aggregates of chlorite whithin quartzitic band. Iňačovce-3 borehole (2305 - 2308 m, sample 24, Tab. 1). Magnif. 24.5 x (plane-polarized light). Fig. 4 - BSE image of fan-like chlorite aggregates associated with chloritoide, quartz and Fe-carbonates. Senné-2 borehole (3282 - 3282.5 m, sample 38, Tab. 1). Magnif. 200 x. Fig. 5 - Mesh texture of lizardite-chryzotile serpentinite from the Senné-8 borehole (3434.5 - 3436 m). Magnif. 48 x (crossed polars). Fig. 6 - Serpentinized peridotite with relicts of primary minerals (OPx). Zbudza-1 borehole (2803 - 2808 m). Magnif. 48 x (crossed polars). Fig. 7 - Tremolite fibres in strongly altered talc-carbonate rock (metaultramafite). Senné-8 borehole (3432 - 3436). Magnif. 24.5 x (plane-polarized light).

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9th International Ceramic Congress on Research for Production (9th CERP)

Welcoming around 300 participants the *Annual meeting* of the *Italian Ceramic Society* for 1993 was held on 4 - 6th October in Rimini with its substantial and integral part, the *9th CERP*.

In present uncertain economic situation when also ceramic industry suffers from production stagnation and reduction, the representatives of the Italian Ceramic Society decided to set for main goals of the Congress such research activity directions which will both support innovative processes and contribute to production revival. It is more than natural, when it is realized that Italy participates approximately in one half of the world production and trade of all ceramic production branches. Organizers prepared three sessions covering different topics in the framework of the annual meeting of the Italian Ceramic Society. Leading personalities in individual sectors of activity, in ceramic and other fields discussed the latest topics in:

1 - Interconnections between basic research and industrial research in traditional ceramics and advanced ceramics: prospects for future research.

2 - Technological innovation: product-oriented or technology-oriented?

3 - Overall economic problems facing the industrial sector and their effect in ceramic field.

The conference programme takes up the *CERP's* central theme, "Ceramic Research for Production". Within the theme the attention was focused on three topics:

1 - Raw materials: Wall and floor tiles. Sanitaryware. Tableware and technical ceramics. Refractories. Bricks.

2 - Process innovation: Raw material processing equipment. Shaping. Drying systems and equipment. Surface treatement (colour, silk-screen printing, etc.). Firing. Finishing. Randling and storage. Automatic production lines. Measurement controlling and inspection.

3 - Special session: Ceramics at high technology.

In the Raw materials section a contribution drew attention dealing with Turkish ceramic raw materials since there has been a considerable progress in mining and processing of the materials in this country. Mainly deposits of kaoline, halloysite, bentonite, feldspars, quartz, wollastonite, talc, pyrophyllite and zeolite minerals (clinoptilolite and mordenite) are concerned here. The deposits occurring in Neogene sediments have great resources and favourable technological properties and are used in many applications: fillers, glass and flux makers, viscosity reductors, special formers and materials for prevention the environmental pollution.

Much attention was also given to the possibilities of mining and dressing of Italian sodium-potassium feldspars for vitrified stoneware and glazes. A reduction of iron oxides contents from 1.3 % to 0.12 % is achieved by magnetic separation in the case of Piedmontese high feldspar granite. In general, it can be stated that Italian granites with high contents of feldspars produce high-quality raw materials for both the ceramic and glass industries.

Our participation in the 9th CERP made it possible to present new knowledge on Slovak raw materials for ceramics dealing with kaolines (Horná Prievrana), kaolinite clays and sands (Gregorova Vieska and Vyšný