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TO THE LITHOLOGICAL-GEOCHEMICAL CHARACTERIZATION OF UPPER TRIASSIC-LOWER JURASSIC SEDIMENTATION (KRÍŽNA-NAPPE, WEST TATRA MTS.)

(Tabs. 3, Figs. 3)

Abstract: On the basis of the lithological character, manometric analyses, analyses of microelements (B, V, Cu, Pb, Sr, Ba, Cr, Co, Ni), content of clay minerals and some accessory minerals in the series of samples, in regular intervals taken from the Upper Triassic — Lower Jurassic sequence of sediments of the Krížna Nappe in the West Tatra, it was possible in a considerable extent to complete he conception about properties of the sedimentary environment, reconstructed on the basis of biofacial and lithofacial characterization (A. Gaździcki et al., 1979). Surprising are mainly the data about horizons with the contents of detrital chrome spinels and zircon, chlorite and muscovite and with high concentrations of Ba, Sr and V.

Резюме: На основе литологического характера, манометрических анализов, анализа микроэлементов (B, V, Cu, Pb, Sr, Ba, Cr, Co, Ni), содержания глинистых минералов и некоторых акцессорных минералов в серии проб, в регулярных интервалах отобранных из верхнетриасово — нижнеюрской последовательности осадков крижнянского покрова в Западных Татрах было возможным в значительной степени дополнить представление о свойствах осадочной обстановки реконструированной на основе биофациальной и литофациальной характеристики (А. Гажджицки и др., 1979). Поразительны именно данные о горизонтах с содержанием детритовых хромшпинелей и циркона, хлорита и мусковита и с высокими концентрациями Ba, Sr и V.

Introduction

The Triassic and Jurassic sediments of the Krížna Nappe in the West Tatra Mts. are present in the characteristic basinal ("Zliechov" in sence of M. Maheľ) development. Moreover the sequence taking part in the geological structure of this area, are for West Carpathian conditions very well exposed. The profile Nad poslednou lúkou (Above the last meadow) in the Juráňová dolina valley was chosen for detailed lithological and geochemical valuation just owing to the fact that the continuous bed sequence from Upper Triassic (Norian — Rhaetian deposits of the Carpathian Keuper, Upper Rhaetian Fatra Formation), up to Lower Jurassic deposits (Hettangian — Lower Sinemurian Kopienec Formation, Sinemurian-Domerian Janovky Formation), well characterized by macro- and microfauna (A. Gaździcki et al., 1979) and lithostratigraphically well investigated, is uncovered in details. From horizons of the 220 m long profile

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were selected on the whole 41 samples, which were subjected to further laboratory treatment.

Roughly 2 kg samples were dressed into fraction < 0.09 mm. From it was taken the average sample for determination of the share of carbonates by manometric method by J. Turan — L. Vančová, 1972, (carried out by J. Turan, Geological Institute of the Comenius University, Bratislava). By further crushing into fraction < 0.063 the sample was prepared for spectrochemical analysis of B, V, Cu, Ba, Sr, Co, Ni by the method of J. Medveď — E. Plško — J. Cubínek, 1974 and J. Medveď — J. Kubová — E. Plško, 1979. The analytical results were correlated with standard reference materials of the Zentr. Geolog. Institut, GDR (ZGI-KH: limestone, ZGI-GM: granite), Fred. Smith Chemical Co. (GFS 401-limestone), National. Bureau of Standards (NBS-88-a: dolomitic limestone, NBS-1-b: marly limestone), I. S. Geol. Survey (G-2: granite) as well as with recommended values in F. J. Flanagan, 1973; E. Thomson et al., 1970, at which a satisfactory agreement can be stated. The fraction 2 μ was separated from shaly horizons by Andreasen's method (J. Konta, 1957). For distinguishing minerals of the chlorite and kaolinite group the samples were annealed at 450 °C, for identification of minerals with mixed illite-montmorillonite structures glycerine was used. Diffraction records were elaborated by E. Šamajová (Geol. Institute of the Comenius University, Bratislava).

Mineralogical composition

The study of mineralogical composition of the individual horizons was mainly based on microscopical observation and manometric determination of the share of calcite, dolomite and non-carbonate remnant, completed (mainly in clay horizons) by analysis of X-ray diffraction record of clayey fraction and analyses of heavy mineral grains. The rocks of the preponderant majority of horizons can be, according to the classification of M. Mišík (1970) and J. Konta (1973), classified as various transitional types of the sedimentary order claystone — limestone — dolomite (see Tab. 1.) The carbonates of horizons of the Carpathian Keuper and basal beds of the Fatra Formation can be mostly valuated as clayey-, clayey calcareous (marly)- and calcareous-clayey dolomites with variable share of sandy fraction. The content of $CaMg(CO_3)_2$ in them varies from 43.55 to 62.55 %. Also the clayey rocks of these formations have a higher portion of $CaMg(CO_3)_2$ (on an average 22.64 %), whilst the portion of $CaCO_3$ is relatively low (3.15 %). The carbonates of Fatra- and Kopienec Formations are represented by various transitional types of limestones with variable $CaCO_3$ content (from 61.65 to 78.74 %, in highly sandy horizons at the boundary of both formations the content of $CaCO_3$ sinks below 40 %). The X-ray diffraction analysis has indicated that the main clayey mineral in all investigated samples (see Tab. 2) is illite. In samples from horizons of the Carpathian Keuper was established a more distinct portion of kaolinite, which, however, gradually decreases toward the overlier (in less measure it is still present in shaly intercalations between limestone horizons of the Fatra Formation). In the higher part of the Fatra and Kopienec Formations minerals of the chloritoid group are found, forming often even small concretionary nodules, galls or thin beds of ooids. Between horizons 398 to 413 chlorite can be usually observed optically in thin sections. Elsewhere, where the mineral is finer dispersed in the ground mass of the rock, it was possible to distinguish it from kaolinite by annealing of samples at 450 °C (mainly the horizons 337 and 406). In the upper part of the claystone sequence of the Kopienec formation chlorite is more rare. However, mixed structures of clay minerals, pointing to the presence of montmorillonite group minerals, were established. In qualitative composition of the associations of clay minerals from intercalations of clay rocks of the sequence thus gradual replacement testifying to a gradual change of the sedimentary environment with paleogeographical development of the area, can be stated: more distinct representation of kaolinite in horizons of the Carpathian Keuper, chlorites at the boundary of the Fatra- and Kopienec Formations and montmorillonite in the higher part of the Kopienec Formation indicate the development from the terrestrial basin with marine floods through a shallow-marine basin to a stable marine basin in the region of deeper neritic (more in detail see next).

Heavy minerals were studied optically in thin sections, as well as also after separation from the insoluble residue. In separation of the insoluble residue 15-% hydrochloric acid was used, epigenetic pyrite was dissolved in 20 % nitric acid.

The clastic admixture, which occurs in horizons of the Carpathian Keuper, is composed of aleuritic quartz grains. Only sporadically small grains of heavy minerals, fragments of rocks (mainly dolomite and limestone) and pseudomorphs after evaporite minerals appear. In the upper part of the basal beds of the Fatra Formation the clastic admixture totally vanishes and appears in the upper part of the "upper biostrom" again (of. Fig. 1). In this part of the profile the clastic admixture attains 15—20 (sporadically up to 60) per cent of rocks volume. The maximum of clastic admixture is in basal clastics of the Kopienec Formation (horizon 409:96 %). The association of heavy minerals is in all this section equal, although their mutual ratio and per cent representation in individual horizons change. In the basal clastics of the Kopienec Formation (horizons 409, 412) tourmaline highly predominates (tourmaline 65 %, rutile 15 %, zircon 12 %, magnetite 4 %, clastic chlorite 1 %, ilmenite, spinel,? corundum and further unidentified minerals 3 %). The chemical character of the association of heavy minerals together with the amount of muscovite and sericite, accumulated in interbedded and inner-bed laminae distinctly influences the chemical curve of boron concentration (Fig. 2).

In the light fraction besides usually undulatory quartz, muscovite, sericite, plagioclase and potassium feldspar were observed. The grains and crystals of heavy minerals are weakly worked up and neither indicating a longer transport, nor reworking of older sediments. Their association testifies to the presumption, that their main source have been probably metamorphosed rocks. The source of spinels, which should be an unknown body of ultrabasics, remains questionable.

Distribution of microelements

As a great part of microelements is adsorbed mainly by clay minerals, in sampling we were directed to layers and intercalations of clayey rocks or to rocks with more distinct clay admixture. However, also in common carbonate rocks of the profile the portion of non-carbonate remnant, the bearer of clay component is sufficiently high (25.18 % in dolomites of the Carpathian Keuper, 21.22 % in carbonates of the Fatra Formation and 16.83 % in limestones of the

Table 1
Manometric and spectral analyses of microelements of the profile

Sample	Rock	% $CaCO_3$	% $CaMg CO_3$	% IR	B	Pb	V	Cu	Ni	Co	Cr	Ba	Sr
267	sandy, dolomitic claystone	1.32	28.0	70.68	360	16	72	9	68	16	55	141	91
268 A	highly sandy dolomitic claystone	2.67	14.79	82.54	263	12	71	13	47	12	83	430	360
268 B	sandy dolomitic claystone	2.24	12.70	85.06	320	18	79	13	47	11	76	450	320
269	clayey dolomite	9.68	62.55	27.77	146	14	4	10	135	4	30	174	126
270 A	sandy claystone	1.99	7.32	90.69	630	30	74	10	76	21	80	245	115
270 B	clayey-calcareous dolomite	23.49	61.76	14.75	55	13	5	14	11	5	14	500	410
271 A	sandy dolomitic claystone	8.17	39.12	52.71	309	12	55	7	46	16	93	200	155
271 B	calcareous-clayey dolomite	13.0	59.55	27.45	66	13	21	6	22	12	45	135	239
272 A	sandy dolomitic claystone	2.24	32.42	65.34	245	21	59	6	59	9	115	129	195
272 B	sandy calcareous-clayey dolomite	16.65	56.56	26.79	46	11	6	9	8	4	14	60	123
273 A	sandy dolomitic claystone	6.54	31.53	61.93	370	14	129	43	83	28	55	980	98
273 B	sandy clayey dolomite	9.77	49.04	41.19	72	9	14	7	28	5	35	33	186
274 A	sandy claystone	—	7.74	92.26	470	15	86	27	89	27	112	148	195
274 B	sandy clayey-calcareous dolomite	36.75	51.04	12.21	41	14	7	6	10	3	514	123	1500
277 A	sandy dolomitic claystone	3.22	30.13	66.65	410	6	126	19	60	19	65	62	107
277 B	highly sandy clayey-calcareous dolomite	29.65	43.55	26.80	98	11	7	11	13	3	23	62	355

280	calcareous-clayey dolomite	15.09	60.17	24.74	50	9	3	8	11	3	13	44	440
281	clayey-calcareous dolomite	26.62	48.69	24.69	69	10	145	7	23	9	12	15	234
284	claystone	5.66	5.59	88.75	710	39	123	27	101	39	95	186	204
290	dolomitic claystone	9.50	12.30	78.20	100	6	65	11	17	8	57	120	280
318	dolomitic-calcareous claystone	15.20	12.50	72.30	250	12	106	27	42	16	90	140	210
320	dolomitic-clayey limestone	49.93	20.64	29.43	68	10	123	6	22	8	47	45	14
329	clayey-dolomitic limestone	73.71	16.11	10.18	16	3	2	5	7	2	4	9	282
337	calcareous claystone	43.80	5.70	50.50	77	2	48	10	15	5	38	70	390
342	dolomitic limestone	78.74	10.43	10.83	34	8	3	5	10	2	9	10	300
350	clayey limestone	77.30	9.90	12.80	21	2	18	13	6	2	20	30	460
369	dolomitic-clayey limestone	75.20	11.30	13.50	9	2	10	9	2	2	10	30	530
377	dolomitic-clayey limestone	78.64	10.53	10.83	10	2	13	8	4	2	13	30	410
390	claystone	3.20	1.62	95.18	760	39	117	17	68	21	129	239	120
393	weakly sandy clayey limestone	61.65	8.43	29.92	20	8	16	85	3	2	10	20	560
396	weakly sandy calcareous claystone	15.90	1.80	82.30	87	10	70	13	19	13	53	70	410
402	sandy calcareous claystone	70.41	10.0	19.5	11	2	12	10	3	2	11	50	640
406	highly sandy dolomitic-clayey limestone	39.84	23.53	33.63	10	19	460	8	30	17	191	24	525
409	sandy claystone	0.64	—	99.36	525	112	219	22	117	63	101	245	126
413	sandy calcareous claystone	21.95	4.75	73.30	166	51	320	13	66	27	87	159	141
414	dolomitic-clayey limestone	69.52	15.01	15.47	34	2	3	6	10	2	9	22	350
417	clayey-dolomitic limestone	67.22	17.23	15.55	30	10	16	6	13	2	25	22	450
422	dolomitic-calcareous claystone	38.2	10.3	51.50	70	10	104	11	25	10	62	130	360
429	clayey limestone	65.2	9.30	25.50	70	2	46	9	15	3	28	60	670

Remark: the values of spectral analysis of microelements are in $g.t^{-1}$; IR – non carbonate residue

Table 2
Composition of clayey fraction of some claystones in the profile

	Sample	Illite	I—M	Kaolinite	Chlorite
Kopienec Formation	422 413 409	XX XX XX	X X X		X X X
Fatra Formation	406 390 337 284	XX XX XX XX		X X X X	XX X XX
Carpathian Keuper	277 A 274 A 270 A 269	XXX XXX XXX XXX		XX XX XX XX	

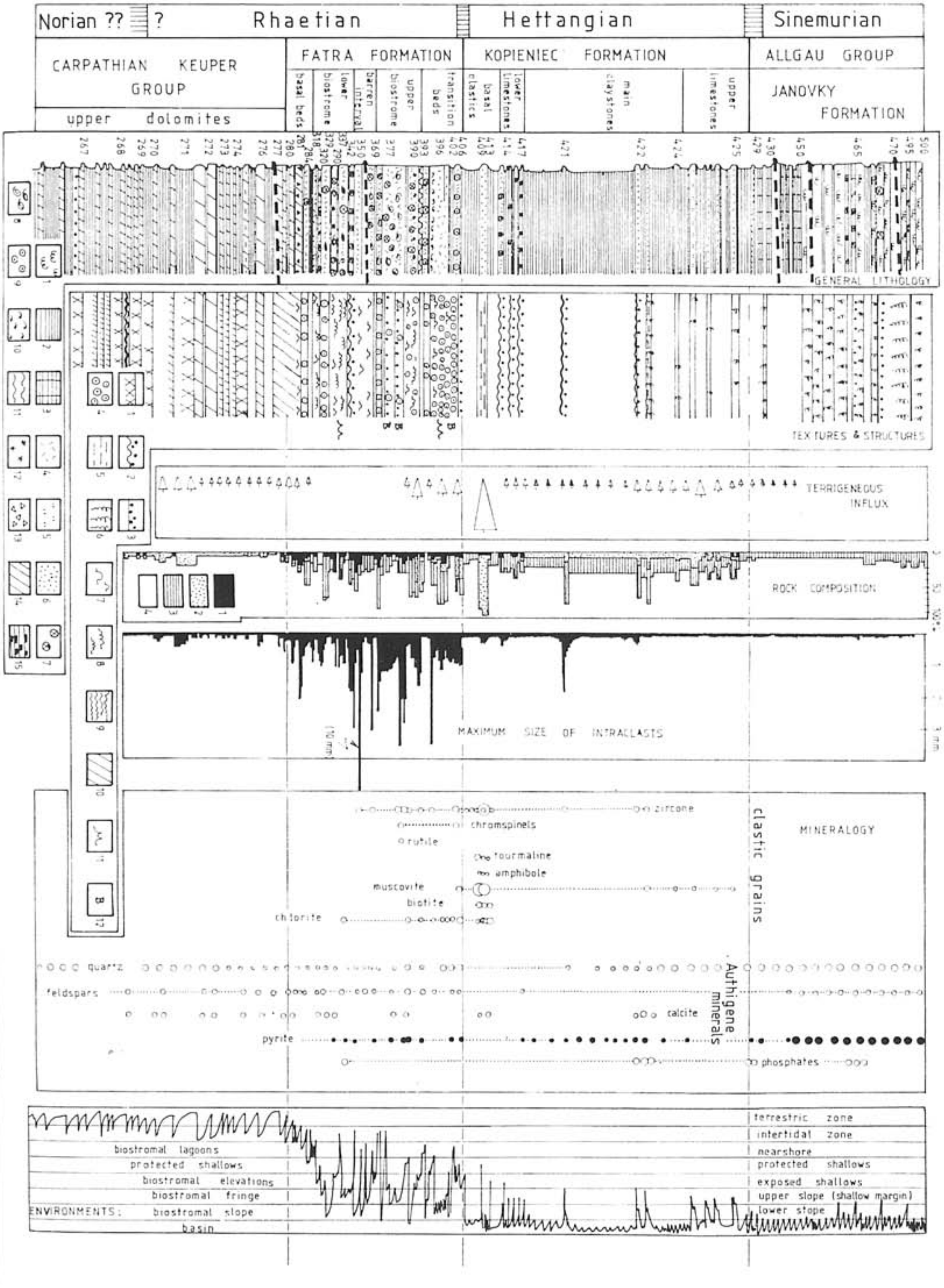
Explanations: I—M (illite-montmorillonite); XXX – distinct content; XX – less distinct content; X – indistinct content

Kopienec Formation) for tracing of the portion of microelements bound to clay minerals.

B o r o n

This element belongs among important microelements of sedimentary rocks from several viewpoints. The essential amount of B of hypergenic zone accumulate in

Fig. 1. Distribution of sedimentological, lithological and mineralogical data of the traced profile Nad poslednou lúkou (Above the last meadow) in the Juráňova dolina-valley, West Tatra.
The first column: chronostratigraphic and lithostratigraphic division, used in A. G a ź d z i c k i et al., 1979.
Second column: general lithology. *Explanations:* 1 – spotted limestones, 2 – marls and claystones, 3 – marlstones, 4 – organodetrital limestones, 5 – aleurites, 6 – sandstones, 7 – crinoidal limestones, 8 – brachiopod limestones, 9 – oolitic limestones, 10 – shelly limestones, 11 – pseudonodular limestones, 12 – coral limestones, 13 – limestone breccia, 14 – dolomites, 15 – layers of dolomite concretions in Keuper claystones.
Third column: structures and textures. *Explanations:* 1 – caliche, 2 – wash-outs with graded bedding of overlying horizon, 3 – gradations without distinct erosion of the substratum, 4 – ooids, 5 – parallel bedding, 6 – bioturbation, 7 – onkolite coatings to crusts, 8 – biostromal growths, 9 – loferites, algal mats, 10 – dolomite crusts, 11 – ripple-marks bedding, 12 – borings (boring of the substratum).
Fourth column: terrigenous influence. The size of arrows means the amount of supplied clastic terrigenous material.
Fifth column: composition of rock (in per cent). 1 – intraclasts, 2 – quartz sand, 3 – allochems, 4 – micritic calcite.
Sixth column: maximum size of intraclasts (in millimeters).
Seventh column: representation of clastic and authigenic minerals.
Eight column: interpretation of the sedimentation environment of individual horizons.


Norian ??
?
Rhaetian
Hettangian
Sinemurian
CARPATHIAN KEUPER GROUP
upper dolomites
FATRA FORMATION
basal beds
lower biostrome
barren interval
upper biostrome
transition beds
KOPIENIEC FORMATION
basal clastics
lower limestones
main claystones
upper limestones
ALLGAU GROUP
JANOVKY FORMATION
GENERAL LITHOLOGY
TEXTURES & STRUCTURES
TERRIGENEOUS INFLUX
ROCK COMPOSITION
MAXIMUM SIZE OF INTRACLASTS
MINERALOGY
zircone
chromspinels
rutile
tourmaline
amphibole
muscovite
biotite
chlorite
clastic grains
quartz
feldspars
calcite
pyrite
phosphates
Authigene minerals
biostromal lagoons
protected shallows
biostromal elevations
biostromal fringe
ENVIRONMENTS:
biostromal slope
basin
terrestric zone
intertidal zone
nearshore
protected shallows
exposed shallows
upper slope (shallow margin)
lower slope

clayey rocks (in our profile the coefficient of correlation B and non-carbonate remnant is r = 0.82). V. M. Goldschmidt – C. Peters, 1932 pointed to the property of the concentrations of B in sediments to reflect the salinity of the sedimentatary environment. Although H. Harder (1959, 1961), A. F. Frederickson – R. C. Reynolds (1960), R. C. Reynolds (1965), G. Ataman (1967), C. T. Walker (1968) and other authors pointed to the complicated dependence between accumulation of B in sediments and paleosalinity, several authors have tried up to now to seek in the analyses of the content of this element for the key to an unambiguous distinguishing of freshwater, brackish, marine and hypersaline environments, others, regarding to the failure in interpretations, totally undervalue the importance of analysing of the B content for paleosalinity and paleo-environmental analyses. D. H. Porrenga (1975) and further authors have stated, that besides paleosalinity the amount of B in sediment depend at least on ten factors. Four of them belong to the characteristics of the sedimentation environment:

1. concentration of B in the environments (H. C. Whitehead – J. H. Feth, 1961),
2. the temperature of the environment (F. J. Dewis – A. A. Levinsson – P. Bayliss, 1972),
3. the length of the time of contact with the environment, e. g. rate of sedimentation (S. Landergren, 1945; D. Heling, 1967),
4. the amount of "inherited" boron (T. H. Adams – J. R. Haynes – C. T. Walker, 1965, or T. W. Bloxan – T. R. Lynn, 1969). The further five factors influence the composition of the substratum,
5. mineralogy of the sediment (R. J. Moore, 1968; H. Harder, 1970; I. Kraus, 1975),
6. content of potassium in illites,
7. grade of crystallinity and amount of amorphous material (S. Landergren, 1945),
8. distribution of size of particles (C. Mosser – J. Call – Y. Tardy, 1972),
9. presence of organic material (C. D. Curtis, 1964; R. M. Eagar – D. A. Spears, 1966).

The last, tenth factor is the diagenesis, which together with metamorphism is effective postsedimentary (H. Harder, 1961; M. Marková, 1972). The interpretation of B concentration in sediment is thus a complex problem, reflecting the whole series of possible, mutually often influencing and completing causes. Only after gradual elimination of their possible effects the dependence of concentration of this element on the paleosalinity of the sedimentation environment can be traced.

The average content of B in carbonates (46.47 g. t^{-1}) and in clayey rocks of our profile (340 g. t^{-1}) is relatively high. Although in the samples from the Carpathian Keuper and Fatra Formation the B content varies very much, on the whole it gradually sinks toward the overlier (Fig. 2). The anomalous high content of B in basal clastics of the Kopienec Formation is caused by concentration of muscovite in intercalations between sandstone banks. The gradually sinking concentration of this element from the Carpathian Keuper to Liassic sequences is probably connected with the changes of paleosalinity but also with decreasing preferential position of illite in the spectrum of present clay minerals. The high content (75 g. t^{-1}) of B in the dolomites of the Carpathian Keuper can be connected with the higher portion of non-carbonate remnant, but can also reflect the influence of the hypersaline environment, in which intercalations of clayey rocks, originating in similar environments, formed (C. T. Walker, 1968).

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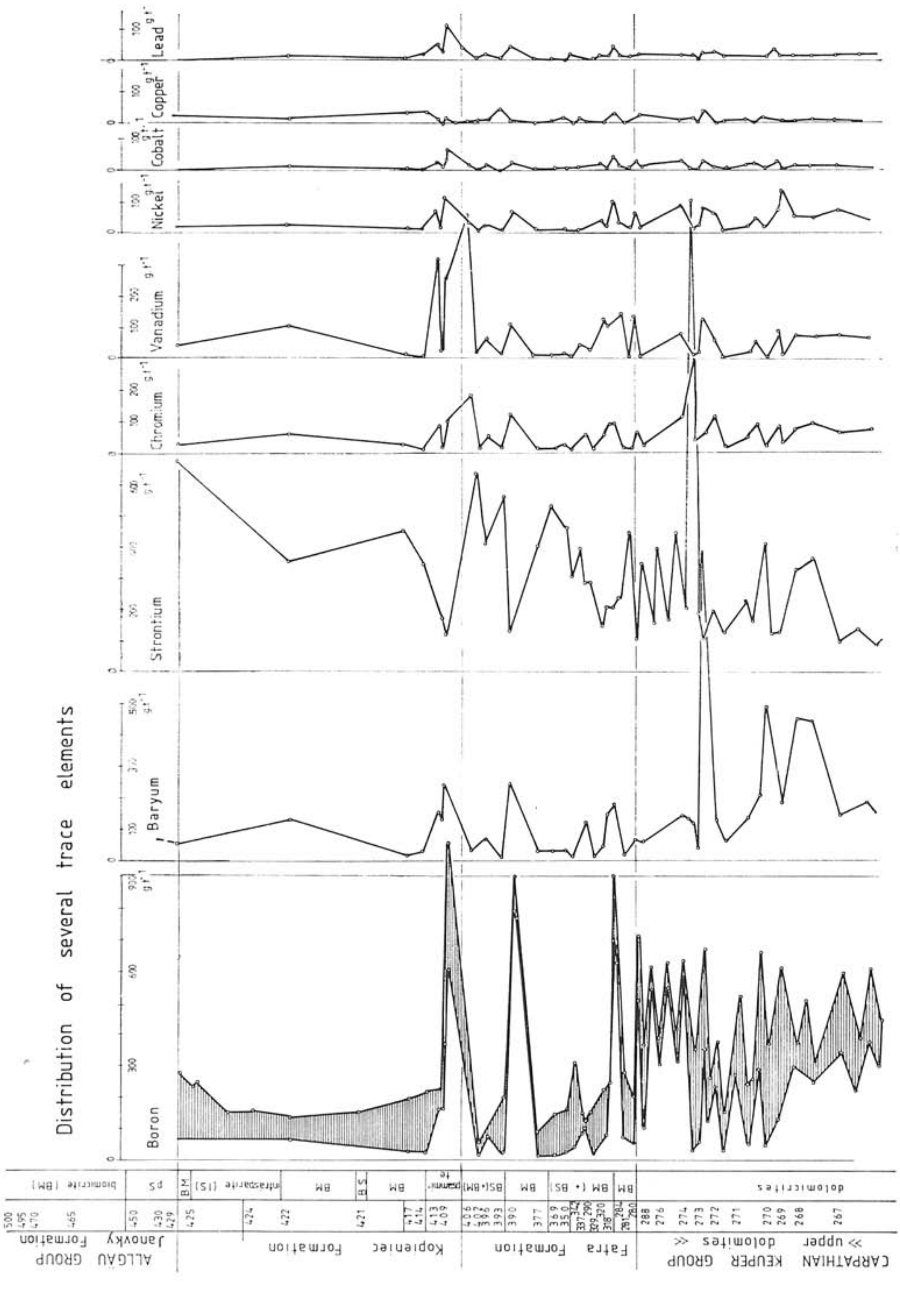
Fig. 2. Distribution of some trace elements in horizons of the described profile. Abbreviations of rock types: BM: biomicrite, BS: biosparite, IS: intrasparite, pS: pseudosparite.



Distribution of several trace elements

V a n a d i u m

The correlation between V content and non-carbonate remnant ($r = 0.43$) testifies to the assumption about the bond of this element to clay particles. In greater amount V accumulate in clayey sediments of stagnant marine basins (G. E. R e i n s o n, 1977). Not a little rôle plays also the bond of vanadium to organic carbon.

The average value of concentration of V in claystones of our profile is 107 $g.t^{-1}$ (in carbonates 44.5 $g.t^{1-}$). Its content increases to the overlier: the claystones of the Carpathian Keuper contain 83 $g.t^{-1}$ (the clayey rocks of the Fatra Formation 88 $g.t^{1-}$), the claystones of the Kopienec Formation 214 $g.t^{-1}$ vanadium (Fig. 2). The last of the averages is, however, influenced by remarkably high V-concentration in basal clastics of the Kopienec Formation (samples 406, 409, 413) where is equally also a higher content of Co, Ni and Cr. Less anomalies of concentration are in the clayey horizon 390 and in the basal beds of the Fatra Formation (horizon 284). Vanadium concentrated in a reductional sedimentary environment, where in the sediment an amount of organic matter accumulated and clusters of pyrite formed. Correlation of V with Cu is highly positive (r for claystones of the Carpathian Keuper is 0.81 and for clayey rocks of the Fatra Formation even 0.84).

C o p p e r

At this element is also emphasized its bond to particles of clay minerals and organic matter (D. M. H i r s t, 1962; G. E. R e i n s o n, 1977). The correlation coefficient of Cu and noncarbonate remnant in the horizons of our profile is, however, 0.23 only. The average content of Cu in clayey horizons of the profile is 16.5 $g.t^{-1}$, in carbonates 11.8 $g.t^{-1}$; the horizon of the marly limestone 393, however, contains 85 $g.t^{-1}$ of copper! The higher content of Cu is bound to products of a reductional environment with concentrations of organic matter with formation of sulphides (pyrite).

L e a d

In marine sedimentary rocks lead is found usually in dispersed state only. The concentrations of Pb, Zn and Cd are cleared up by syngenetic volcanic activity (H. J. S c h n e i d e r, 1964). The Pb-Zn environment is bound to hypersaline and weakly euxinic back-reef facies rich in clay minerals. The highest concentrations of Pb (about cca 80 $g.t^{-1}$), however, are mentioned from deep-marine clays (J. F. M a r s h a l l, 1980).

The coefficient of correlation between the content of Pb and non-carbonate remnants in the described profile is 0.56. Its average content in clayey rocks of the profile is 23.6 $g.t^{-1}$, in carbonates 8.3 $g.t^{-1}$. The distribution of Pb in the horizons of the profile is generally equal (Fig. 2). The local increasing of Pb content in basal beds of the Kopienec Formation (Tab. 3) is obviously caused by clastic supply.

S t r o n t i u m

Barium and strontium belong among the most abundant trace elements of the lithosphere. On the contrary to several other authors D. M. H i r s t (1962) thinks that the distribution of Sr need not be always controlled by calcium only: Sr can be also adsorbed by clay minerals, mainly in environments with higher salinity (P. E. Potter et al., 1963). O. H. Pilkey – J. Hower (1960), however, prove that the relations between salinity and Sr content are more complicated than this element could be an indicator of paleosalinity. J. R. Krantz (1976), on the contrary, considers Sr as a good indicator of facial and diagenetic conditions for sediment formation. He mentions, however, that its content in the sediment can be considerably changed by washing out by water during diagenesis and recrystallization of aragonite into calcite. The high content of Sr (and occurrence of celestite) indicates evaporite-forming conditions in the aride environment (cf. also A. T. Wells, 1980).

The geochemical linking of Sr with carbonates is expressed by the high value of correlation ($r = 0.46$). The average content of Sr in carbonates of the profile is 419.2 $g.t^{-1}$, in clayey rocks 215.4 $g.t^{-1}$. The conditions of the origin of anomalous concentration of Sr in the horizon 274 of the Carpathian Keuper (1500 $g.t^{-1}$) could be analogous to the environment of formation of evaporite horizons with celestite in the Raibl Group of the Alps (J. R. Krantz, 1976).

Barium

It accumulates mainly in hydrothermal products in the continental part of the earth crust. In hypergene stage is it isomorphous with K but also with Cs and Sr (A. T. Wells, 1980). The highest concentrations in hypergene environments (2300 $g.t^{-1}$) it reaches in deep-marine clays (K. K. Turekian – K. H. Wedepohl, 1961) or in hypersaline supratidal environments (A. T. Wells, 1980).

Z. A. Janočkina (1966), setting out from the supposition, that different migration of Sr and Ba in the hypergene stage reflects the changes in the of character of sedimentation environment, considers the sediments with the value of ratio Sr/Ba > 1 as freshwater, higher values have to be typical for marine sediments. For comparison, in our profile from sixteen samples of the Carpathian Keuper the half have this ratio < 1, whilst from 23 samples of the Fatra- and Kopienec Formations only four have this ratio less than 1.

The average content of Ba in our profile is relatively low (in clayey rocks 230 $g.t^{-1}$, in carbonates 71 $g.t^{-1}$). The higher content of Ba in the Carpathian Keuper (in claystones from 62 to 980, on an average 230 $g.t^{-1}$) can be ascribed partly to a distinct portion of illite in composition of claystones, but also to replacement of calcium in evaporite minerals by barium.

Chromium

The main part of Cr released with weathering, is mainly bound to secondary layered silicates, mainly illite and montmorillonite (D. M. Hirst, 1962). G. O. Nichols – D. H. Loring (1962) deny the dependence between the content of Cr in sediments and the presence of sulphides and carbonates.

In our profile the low value of correlation ($r = 0.21$) does not indicate the existence of dependence between Cr content and non-carbonate remnant. The average Cr content in claystones is 80.8 $g.t^{1-}$ in carbonates 51.3 $g.t^{-1}$. A higher Cr content, in dolomites of the Carpathian Keuper (horizon 274: 514 $g.t^{-1}$) is accompanied by increasing Ba and Sr contents (see Tab. 1, Fig. 2).

Table 3

Correlation matrixes and fundamental statistical

	Carpathian Keuper — dolomites									Fatra Formation —			
	B	Pb	V	Cu	Ni	Co	Cr	Ba	Sr	B	Pb	V	Cu
B	1									1			
Pb	0.14	1								0.34	1		
V	- 0.21	– 0.23	1							0.03	0.84	1	
Cu	0.23	0.06	– 0.63	1						– 0.16	0.04	– 0.14	1
Ni	0.87	0.36	– 0.24	0.07	1					0.52	0.87	0.85	– 0.3[illegible]
Co	– 0.12	0.11	0.86	– 0.36	– 0.07	1				0.22	0.87	0.97	– 0.19
Cr	– 0.39	0.44	– 0.10	– 0.49	– 0.20	– 0.25	1			– 0.15	0.79	0.95	– 0.12
Ba	– 0.09	0.47	– 0.30	0.69	0	0.06	– 0.11	1		0.09	– 0.12	– 0.07	– 0.14
Sr	– 0.44	0.44	– 0.16	– 0.31	– 0.31	– 0.29	0.96	0.04	1	– 0.75	– 0.18	– 0.02	0.35
AP	74.85	12.14	9.14	9.00	32.42	5.14	96.42	155.28	419.85	28.90	6.81	73.18	14.90
S	36.64	1.86	6.14	2.94	45.79	3.13	184.47	159.87	488.68	23.12	5.32	137.78	23.96
V	48.95	15.35	67.25	32.71	141.23	60.90	191.30	102.95	116.39	79.98	78.11	188.28	156.68
GP	68.46	12.01	7.78	8.60	19.16	4.59	37.76	108.52	284.57	21.80	5.03	18.05	9.44
	Carpathian Keuper — claystones									Fatra Formation —			
B	1									1			
Pb	0.48	1								0.98	1		
V	0.23	– 0.43	1							0.88	0.88	1	
Cu	0.17	– 0.29	0.81	1						0.57	0.56	0.84	1
Ni	0.64	0.25	0.44	0.64	1					0.93	0.93	0.90	0.75
Co	0.62	– 0.06	0.62	0.80	0.84	1				0.83	0.87	0.85	0.77
Cr	– 0.01	0.33	– 0.57	– 0.33	0	– 0.18	1			0.89	0.87	0.91	0.61
Ba	– 0.11	– 0.01	0.45	0.70	0.18	0.34	– 0.44	1		0.93	0.89	0.87	0.52
Sr	– 0.47	– 0.05	– 0.36	– 0.22	– 0.55	– 0.54	0.30	0.09	1	– 0.83	– 0.77	– 0.86	– 0.61
AP	375.22	16.00	83.44	16.33	63.88	17.66	82.55	309.44	181.77	330.66	18.00	88.16	17.50
S	118.50	6.72	26.67	11.94	16.15	6.74	22.19	284.66	98.26	319.89	16.62	31.12	7.73
V	31.58	42.04	31.97	73.14	25.29	38.18	26.88	91.99	54.05	96.74	92.36	35.29	44.22
GP	360.57	14.74	80.08	13.41	62.09	16.52	79.86	226.20	161.44	211.83	11.39	83.26	16.14
	Kopienec Formation — claystones									Kopienec Formation —			
AP	44.66	4.66	21.66	7.00	12.66	2.33	20.66	34.66	490.0	253.66	57.66	214.33	15.33
S	22.03	4.61	22.05	1.73	2.51	0.57	10.21	21.43	163.70	239.83	51.32	108.07	5.85
V	49.32	98.97	101.78	24.74	19.86	24.74	49.42	63.28	33.40	94.54	89.00	50.42	38.21
GP	41.48	3.41	13.02	6.86	12.49	2.28	18.46	30.73	472.55	182.72	38.51	193.88	14.65

Remark: For the small number of samples the correlation matrixes of claystones and limestones of the Kopienec Formation are not mentioned in the survey data of microelements of the profile

limestones					The whole profile — carbonates									IR
Ni	Co	Cr	Ba	Sr	B	Pb	V	Cu	Ni	Co	Cr	Ba	Sr	
					1									0.82
					0.41	1								0.56
					– 0.15	0.47	1							0.43
					– 0.15	– 0.01	– 0.67	1						0.23
1					0.75	0.42	0.09	– 0.11	1					0.68
0.43	1				0.11	0.66	0.82	—0,16	0.20	1				0.75
0.73	0.89	1			– 0.05	0.44	0.24	—0,11	0	0.20	1			0.20
– 0.07	– 0.04	0.01	1		0.31	0.36	– 0.15	– 0.02	0.20	0.08	0.08	1		—
– 0.46	– 0.17	0.10	0.16	1	– 0.33	0	– 0.02	0.10	– 0.29	– 0.19	0.78	0.05	1	—
11.00	4.63	30.90	27.90	399.54	46.47	8.28	44.47	11.80	18.38	4.47	51.28	71.33	419.23	
9.62	4.84	54.29	14.05	179.30	34.21	5.07	102.57	16.94	27.93	3.94	113.02	107.33	302.26	
87.48	104.45	175.66	50.35	44.87	73.62	61.20	230.62	143.51	151.95	88.12	220.39	150.46	72.09	
7.62	3.27	15.71	24.28	307.12	35.00	6.36	13.01	8.74	11.12	3.48	21.53	41.36	318.35	
claystones					The whole profile — claystones									
					1									
					0.45	1								
					0.11	0.67	1							
					0.35	0.15	0.27	1						
1					0.78	0.70	0.46	0.51	1					
0.96	1				0.58	0.87	0.62	0.51	0.86	1				
0.77	0.64	1			0.62	0.46	0.20	0.06	0.55	0.38	1			
0.80	0.66	0.96	1		0.17	0.03	0.06	0.59	0.29	0.18	– 0.07	1		
– 0.73	– 0.58	– 0.93	– 0.96	1	– 0.63	– 0.39	– 0.38	– 0.31	– 0.71	– 0.51	– 0.41	– 0.19	1	
43.66	17.00	77.00	137.50	269.00	340.11	23.61	106.83	16.55	58.05	27.05	80.83	230.22	215.38	
34.7	12.18	33.74	66.45	113.52	213.25	25.67	66.67	9.45	28.99	13.73	24.90	216.08	109.44	
79.48	71.45	43.82	48.32	42.23	62.7	108.72	62.41	57.12	49.94	68.48	30.81	93.83	57.81	
33.43	13.76	70.86	124.13	247.55	269.69	15.87	94.61	14.48	49.91	16.73	77.03	176.88	190.54	

limestones				
69.33	33.33	83.33	178.00	209.00
46.09	27.06	19.75	59.80	130.98
66.47	81.18	23.70	33.60	62.67
57.79	25.71	81.67	171.72	185.62

Explanations:

AP: arithmetic mean
S: standard deviation
VK: variation coefficient
GP: geometric mean
IR: correlation coefficient of the individual microelements of the profile and non-carbonate residue

Cobalt and Nickel

These elements are geochemically closely linked with iron, the concentrations of Co in consequence of its not even proton number, however, are lower. The correlation coefficient of Co ($r = 0.75$) and Ni ($r = 0.68$) with the non-carbonate remnant distinctly indicate linking of these elements with the clayey fraction of sediments. The Co content in the profile is relative low (in clayey rocks on an average 16.7, in carbonates 4.5 $g.t^{-1}$). The higher content of this element in the basal beds of the Kopienec Formation (63 $g.t^{-1}$) can be explained by transport and sorting of clastic terrigenous material.

The average Ni concentrations in carbonates (13.4 $g.t^{-1}$) as vell as in clayey rocks of our profile (58.05 $g.t^{-1}$) correspond to average concentrations of this element in sediments of this type (K. K. Turekian – M. H. Carr, 1960). Co in the profile correlates not only with Ni (in claystones of the Carpathian Keuper $r = 0.86$ and in the Fatra Formation even 0.96!), but also with vanadium (in claystones $r = 0.62$, in carbonates 0.82), with lead (r in claystones 0.87, in carbonates 0.66) and partly also with copper (r in claystones 0.51) and boron (r of claystones 0.58). Ni besides that correlates well with B (claystones $r = 0.78$, carbonates 0.75) and in the Fatra Formation with V (clayey rocks $r = 0.9$, carbonates 0.85), with Pb (claystones $r = 0.7$, carbonates 0.42) and partly with Cu (claystones $r = 0.51$). Remarkable is the correlation of Ba with almost all traced elements from the clayey horizons of the Fatra- and Kopienec Formations. The correlation coefficient is besides Ba-Cu ($r = 0.52$) and Ba-Co ($r = 0.66$) in the Fatra Formation and Ba-V ($r = 0.27$) in the Kopienec Formation always higher than 0.8. But, however, it does not correlate with Sr! The relations of the individual traced elements are clearly conspicuous from the correlation matrix (see Tab. 2).

Interpretation of the sedimentary environment

Carpathian Keuper (Norian-Lower Rhaetian)

The typical development of this sequence is limited to zones, affected by Early-Kimmerian emersion (i. e. the Tatric and Fatric of the West Carpathians). The analysis of lithological composition of horizons, sedimentary structures, mineralogical content and spectrum of present microelements confirms the conclusion, that the sequence sedimented in a continental basin under rapidly changing conditions of the environment (flat waste land to desert with ephemeral water streams and drying -up lakes, affected by occasional short-dated transgressions of shallow sea). The relatively fine – grained, homogeneous sediment of claystones, containing dry-land xerophilous palynoflora and occasional admixture of quartz silt, testify the fact that the main part of terrigenous material was obviously transported by wind. Multiply at the surface of the sediment carbonate crusts of caliche-type developed (Fig. 1). The high content of B (Tab. 1, Fig. 2) testifies to a higher salinity during sedimentation of claystones. The higher content of Ba (horizon 273 A) indicates an environment with formation of evaporite minerals. Dolomite intercalations are accompanied by occurence of remnants of marine plankton (cf. A. Gaździcki et al., 1979) and often by higher of Sr and Cr. Their origin is connected with penetration of marine water during short-timed marine floods. The horizon 274B with extreme concentration of Sr sedimented obviously in hypersaline environment with celestite formation.

Fatra Formation (Upper Rhaetian)

is a product of a shallow-marine basin, which formed during Upper Rhaetian in the Fatric region. The sedimentation here was taking place on mobile substratum, the oscillation movements of which gave rise to the cyclic structure of the sedimentary sequence.

The basal beds-member coincides many points with the underlying horizons of the Carpathian Keuper (Fig. 2). The terrigenous influence in banks of limestone-dolomitic rocks, however, gradually decreased contemporaneously with appearing of marine fauna.

The lower biostrome-member is typical in onset of limestone facies with characteristic marine benthic fauna, stabilizing the substratum surface first with small coatings and crusts, later with more extensive biostromatic constructions. The contents of B and Ba and further microelements in rocks of the horizons gradually decrease.

The barren interval-member is characterized by minimum content of B and Ba and sudden increase of Sr content. Lithologically it is characterized by intercalations of dolomites and redeposited bioclastic rocks. All these features indicate the renewal of conditions of extremely shallow water.

The upper biostrome-member implies the renewal of neritic biostrome sedimentation, finally accompanied by moderately increasing supply of terrigenous material (Fig. 1). Besides clastic quartz gradually appear heavy minerals (rutile, chrome spinels). The representation of chlorite in the spectrum of clayey minerals implies, according to W. E. Parkham (1966), a deeper neritic marine environment in the middle of the basin, distant from the sources of clayey material. In the horizons of the upper biostrome representation of B, Ba, Cr, V and Ni increases again. On the contrary, the portion of Sr sinks.

Greater changes can be observed in the member of transitional beds. The horizon of pseudonodular muddy limestone 393 with higher content of Cu indicates stagnant conditions. On the contrary, the higher horizons contain abundant intraclasts and an amount of biodetritus, testifying to a more distinct current regime of the environment. The share of clastic quartz increases. The vanishing of stenohaline organism indicates salinity changes. This assumption can be supported by a new increase of Sr content. The horizons 405—406 with mixed chamosite, calcite, haematite and chlorite ooids contain anomalous concentrations of Cr, V and Sr (cf. Fig. 3).

Kopienec Formation (Hettangian)

The basal clastics-member of this formation essentially differs in its composition from the underlier. It is formed by greenish brownish-grey claystones with thick intercalation of light-grey quartz sandstones. The sandstones

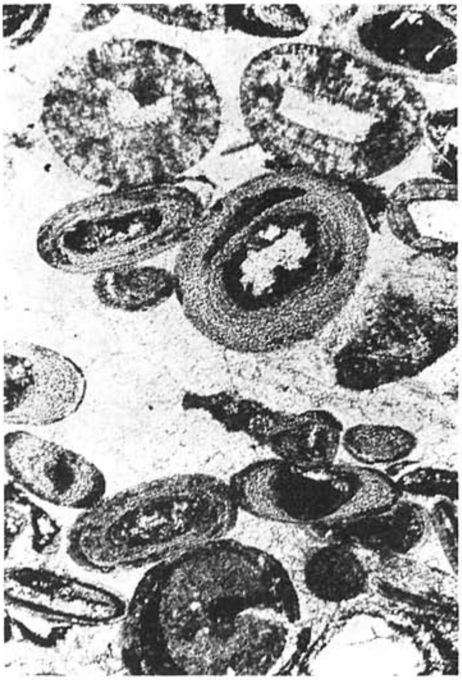


Fig. 3. Thin section from the horizon of oolitic limestone 406. In the figure is a distinct mixture of individual ooid types (calcite, chamosite, haematite). The cores of ooids are formed by clastic quartz, juvenile shells of gastropodes, ossicles of crinoids, fragments of valves of bivalves and other organisms: Magnification: 50 ×.

contain a relatively variegated scale of heavy minerals, also shown in the variegated chemical character of microelements (Figs. 1.2). The laminae between the sandstone layers are formed by an amount of muscovite scales. The higher lying limestone intercalations are characterized by a low content of Sr and higher portion of Ba, Ni and V.

The overlying lower limestone-member is a complex of alternating marlstone and limestone banks. The intercalations if limestones have a gradation texture and represent the bases of erosional cycles. They are relatively poor in fauna, accessory minerals and microelements. During sedimentation of the overlying "main claystones", a moderate increase in Sr. Ba, Cr, V contents can be observed. This part of the profile was, however, sampled already only relatively thinly and therefore no definitive conclusions can be drawn about its geochemical development.

Conclusion

By the study of lithological, mineralogical and geochemical composition of the Upper Triassic to Lower Jurassic bed sequence of the Krížna nappe of the West Tatra Mts., we came to the following conclusions:

1. The rhythmic structure of the Carpathian Keuper is also reflected in its mineralogical composition and in the content of microelements. The horizons with higher concentration of Ba and Sr represent residual products of an extreme environment with accumulation of salt, evaporite minerals and(?) celestite, obviously already leached at present.

2. The onset of marine limestone facies implied stabilization of the specific association of microelements, only disturbed by shallowing connected with regression during the barren interval.

3. The upper biostrome implies the renewal of normal marine sedimentation. With stronger clastic supply in its upper part, in transitional beds and basal

clastics of the Kopienec Formation, the spectrum of heavy minerals, derived from metamorphosed rocks, appears. The grains of chromspinels indicate the presence of ultrabasic bodies in this source region. This change in composition of sedimentary material indicates a paleogeographical-paleotectonic rebuilding of the area linked with the effects of the Early Kimmerian phase in the Fatric of the Western Carpathians.

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