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RELATIONSHIP BETWEEN NATURAL RADIOACTIVE ELEMENTS (Th, U, K) AND TRIASSIC CARBONATE LITHOFACIES IN HRONICUM AND SILICICUM OF MALÉ KARPATY MTS.

(7 Figs., 2 Pls., 1 Tab.)

A b s t r a c t: We have studied the contents of natural radioactive elements (Th, U, K) in Triassic limestones and dolomites of the Malé Karpaty Mts. We distinguished 4 basic facies in the formation: Middle Triassic shallow-water shelf limestones and dolomites, basin and slope pelagic limestones, forereef and reef limestones and dolomites, and Upper Triassic shallow-water limestones and dolomites. A direct dependence between the values of Th and K and the contents of IR has been confirmed. The contents of Th and K are decisive for the bulk gamma-activity of samples with high IR. In carbonates with low IR the decisive influence is that of U, while its contents in the distinguished facies are variable. The values of U vary in a relatively wide range, even though its average values are not anomalously high. The most marked differences in the concentration of U (0.2–6.6 ppm) have been determined in forereef facies, where material from various facial zones was accumulated.

Р е з ю м е: Автори изучали содержание природных радиоактивных элементов (Th, U, K) в триассовых известняках и доломитах Малых Карпат. В формациях различались 4 основных фаций: среднетриассовые мелководные шельфовые известняки и доломиты, пелагические известняки бассейнов и сколонов, дорифовые и рифовые известняки и доломиты и верхнетриассовые мелководные известняки и доломиты. Подтвердилась прямая зависимость между величинами Th и K, и содержанием нерастворимого остатка. Содержания Th и K являются решающими для обшей гамма-активности образцов с высоким Н.О. В карбонатах с низким Н.О. решающим является влияние U, но его содержание в отличаемых фациях меняется. Содержание урана меняется в относительно широком интервале, хотя его среднее величины не аномально высоки. Самые большие разницы в концентрации U (0,2–6,6 ппм) были определены в дорифовых фациях где аккумулировался материал из различных фаций.

Introduction

The aim of the paper is to characterize the distribution of natural radioactive elements in various Triassic carbonate facies. The study of changes in the contents of these elements in relation to petrographic character of rocks allowed us to determine the most important phenomena affecting the distribution of U and Th in carbonates.

The capability of Th to be bound by absorption in the minerals of IR, especially in clay minerals, has been already documented in earlier works (G r a f, 1960; R o g e r s– A d a m s, 1969).

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The capability of U to form complex compounds with carbonate ions increases the mobility of uranium in sedimentation environment (Langmiur, 1978; Graf, 1960; Michard et al., 1987; Sobotovich et al., 1983). In CO_2-rich environments (in solutions) complex compounds of the type $UO_2\,(CO_3)_2^{-2}$ and $UO_2\,(CO_3)_3^{-4}$ are formed (Michard et al., 1987). Sobotovich et al. (1983) suggested the second type of complex compound as the most probable form of uranium occurrence in ocean water containing 3.10^{-6} g/l U.

U enters sediments from marine water as a result of the decomposition of the uranyl-carbonate complex after the chage of U (VI) into U (IV). This process takes place directly in the sediment or on the boundary sea water – sediment. The decomposition of the complex is usually connected with reduction conditions in the environment which can be caused e.g. by the decomposition of organic matter. Direct relationship between the contents of organic matter and U has been determined in clastogenic sediments (e.g. black shales) (Dongarra, 1984). Uranium which comes into marine basins in soluble form is distributed more or less evenly in the water. It is leached from clastogene sediments much more than it is the case with Th (Grigorev et al., 1975; Sobotovich et al., 1983). It is captured in shallow shelf zones in places of accumulation of organic matter (anaerobic conditions) and phosphate sediments, in the direction of main surface water flow from the continents, as well as in deep abyssal parts of sea in considerable distance from the shore (Grigorev et al., 1975; Sobotovich et al., 1983). The above cited authors described the largest uranium concentrations in near-shore, beach sandstones – 6.10^{-4} %. The distribution of U in marine sediments is in comparison with terrestrial ones even. Maximal U contents are in pelagic sediments which are the main concentrators of organic matter and uranium can accumulate in carbonates also due to the presence of phosphates (Grigorev et al., 1975; Altschuler et al., 1958; Starinsky et al., 1982; Šor et al., 1975; Mo et al., 1973). High U concentrations can occur also in environments with evaporite formation. The study of U concentration in brines during salt precipitation has shown that water is enriched in U (Dongarra, 1984).

Uranium in recent carbonates

The study of recent sediments has shown that relatively U-rich carbonates are formed along the continental slope. U concentrates e.g. in corals, which have been studied quite thoroughly from the viewpoint of their U contents (Friedman, 1968; Haglung et al., 1969; Gritzman et al., 1973; Amiel et al., 1973; Mo et al., 1973). Amiel at al. (1973) discovered that U occurs in corals in organic matter absorbed on aragonite skelet and in the aragonite lattice. U forms complex compound with the organic matter (chitin) (Manskaya–Drozdova, 1968). However, organic matter constitutes a negligible part of coral rocks and thus U bound in it cannot affect the bulk concentration of uranium. A negligible amount of uranium is also bound by absorption on the surface of aragonite skelets. The largest part of U is in aragonite lattices, in total 3 ppm (Amiel et al., 1973). Higher concentration than in corals themselves (2 ppm) has been determined in primary aragonite cements (3 ppm) (Gvirtzman et al., 1973). The level of U concentration in low-Mg calcite substituting diagenetically coral aragonite is a function of U content in meteoric water. Haglung et al. (1969) observed that in the process of freshwater diagenesis with Mg-calcite formation the content of uranium can decrease in comparison with the primary content by as much as 50 % due to continuous removal. If the sediment remains in contact with marine water, the content of U remains stabile.

Data on U content in ancient limestones and dolomites are mentioned in literature only sporadically. According to Rogers–Adams (1969) average U contents in carbonates are

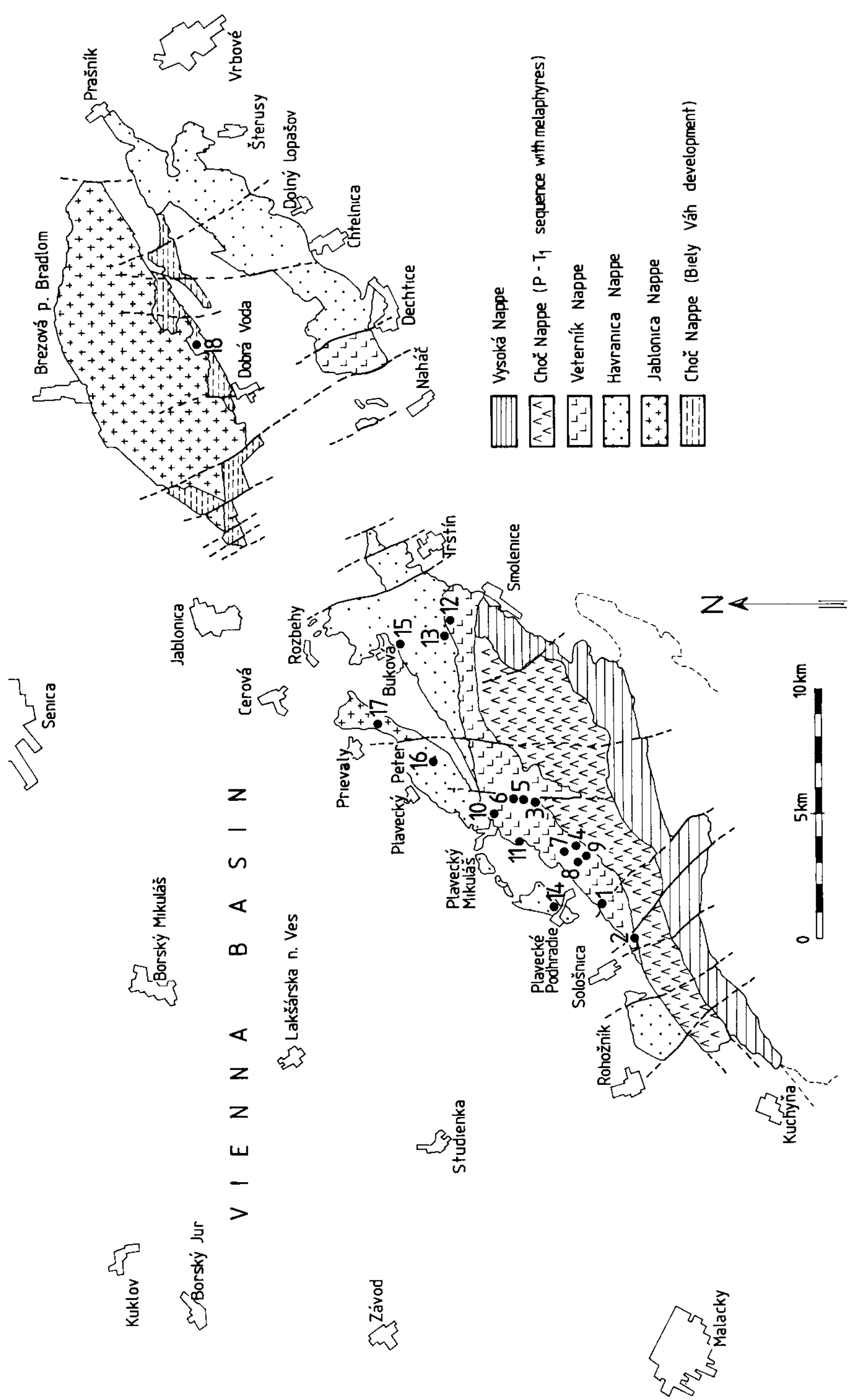

Fig. 1. Tectonic scheme of the studied Malé Karpaty Mts. region. Numbers on the figure localize the profiles marked on Fig. 2.

very similar and vary around 2 ppm. Grigorev et al. (1975) gave the average values 1–1.5 ppm U for carbonates (eastern Kazachstan). Increased contents of uranium have been described in bituminous limestones. E.g. Smyslov (1975) mentioned the values $5-10\times10^{-4}$ % and more. U is bound to bituminous matter.

Geological setting

The region of NE ending of the Malé Karpaty Mts. is formed by nappe bodies composed mainly of Mesozoic rocks (Fig. 1). Above the Vysoká Nappe lies the Choč Nappe formed in the region between the villages Kuchyňa and Smolenice only by Permian and Lower Triassic detrital rocks with melaphyres. Middle and Upper Triassic formations of the Choč Nappe occur in depressions between the Havranica and Jablonica Nappe in the surroundings of the village Dobrá Voda where they have been confirmed by the borehole DV-1 (Fig. 1, No. 18), (Michalík et. al., 1986; Masaryk, 1987; Michalík et al., 1987, Lintnerová et al., 1988).

Above the Lower Triassic of the Choč unit lies the complex of the Veterník Nappe with Middle and Upper Triassic sequences. More to the north (Fig. 1) there are Havranica and Jablonica Nappes, their range being Lower–Upper Triassic. As it can be seen on the scheme Fig. 2, the lithofacial differences between the Veterník, Havranica and Jablonica Nappe are small and it can be assumed that originally they had been one nappe which was later divided by the effects of retrocharriage overthrust faults. Thus the above mentioned nappes and their lithofacial character are similar to the Strážov Unit (Biely et al., 1980).

Sampling and analytical methods

Our sedimentological studies are based on systematic fieldwork and a study of thin sections. The samples were collected on continuous profiles (Fig. 2) perpendicular to the direction of strata. Except these we have additionally studied a few shorter profiles with the aim of determining not only the vertical but as well the lateral distribution of facial zones. The density of petrographic sample collection depended on the facial character and attitude of the rocks. On the basis of a preliminary lithofacial evaluation we collected larger samples (2–3 kg) for geochemical study.

Chemical analysis was carried out by the X-ray fluorescence method on the apparatus Philips PW 1410/20. The obtained results have been applied in the calculation of calcite, dolomite and insoluble residue (IR). Mineralogical characteristics of the rocks and of their IR have been determined by X-ray diffraction (Philips 1050, CuKα). IR was prepared by dissoving the samples in diluted HCl (to 10 %).

The contents of Sr, Mn, Na have been determined by the AAS method, in the part of the rock soluble in HCl (a more detailed description of the method can be found in Lintnerová et al., 1988). The apparatus Perkin-Elmer 2380 was used.

The concentration of natural radioactive elements – Th, U, K – has been determined by a NaI (Tl) single-crystal spectrometer with sample volume of 800 cm^3, having a distinguishig ability of 10.5 % (at ^{137}Cs) and measurement time of 2000 s. The analysis of impulses was carried out by the 1024 channel analyzer NTA-513B (KFKI Budapest). On the basis of repeated measurements of low-active samples we have determined the standard deviation of the concentrations of U – 0.8 ppm, of Th – 0.16 ppm and of K – 0.05 %. The results of the measurements on 170 samples are presented in this paper.

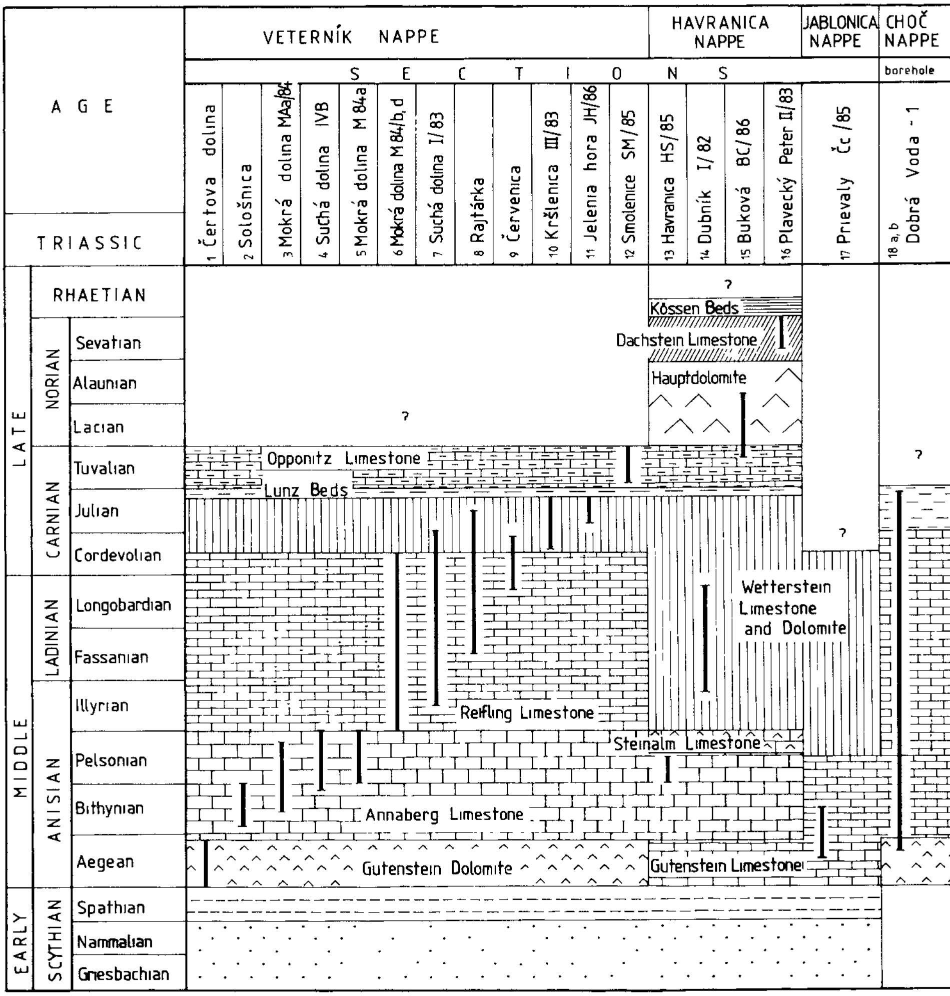

Fig. 2. Lithostratigraphic scheme of Triassic Formations with marked profiles.

Results and discussion

The mineral composition of the studied rocks calculated from chemical analyses as well as the contents of Th, U and K are listed in Tab. 1. The contents of IR in limestone and dolomite samples were mostly relatively low and they did not exceed 10 wt.%.

The studied carbonates formed in the conditions of shallow-water sedimentation with minimal contribution of clastic material. Reifling Limestones which formed in the conditions of intraplatform depressions are characterized by an increased content of silicites – i.e. increased SiO_2 contents. Especially in the formation of Reifling Limestones from the borehole

Table 1

Average values and range of calcite, dolomite, IR, K, Th, U in the observed profiles.

Rock	No. of profile	Number of samples	Calcite	Dolomite	IR	K	Th	U	Uekv.	Th/U
			weith %				ppm			
Gutenstein Limestone	17	7	95.3	3.2	2.5	0.03	0.5	1.7	1.8	0.3
			76.4—98.3	0.5—19.5	1.7—4.1	0.01—0.05	0.4—0.7	1.3—2.2		
Gutenstein. Dolomite	1	5	0.6	96.1	3.2	0.03	0.5	1.9	2.0	0.2
			0.1—3.2	92.5—99.0	1.0—4.1	0.02—0.04	0.3—0.9	1.5—2.5		
Annaberg. Limestone	2	4	96.0	2.4	1.5	0.01	0.6	1.5	1.6	0.4
			94.5—97.6	0.9—3.6	1.1—1.9	0.01—0.02	0.3—1.0	1.3—1.8		
	4	11	95.0	2.5	1.7	0.06	0.6	1.4	1.6	0.4
			93.4—97.8	1.2—3.9	0.9—3.1	0.02—0.26	0.2—1.3	1.2—2.0		
	3	8	95.7	—	4.9	0.05	0.4	1.5	1.6	0.3
			87.6—98.0		2.0—12.3	0.02—0.08	0.1—0.8	1.2—2.0		
	5	4	98.7	—	1.08	0.02	0.5	1.1	1.2	0.5
			96.9—99.35	0.0—0.83	0.7—2.2	0.01—0.03	0.1—0.9	1.0—1.5		
	13	4	96.7	—	3.6	0.01	0.4	1.6	1.8	0.3
			95.6—97.4		2.6—4.4	0.01—0.01	0.3—0.5	1.3—1.8		
Reifling. Limestone	6(b)	5	85.09	—	15.7	0.13	0.8	0.7	1.1	1.1
			72.3—94.9		5.3—37.8	0.04—0.22	0.4—1.1	0.4—1.1		
	6(d)	3	—	—	—	0.01	0.4	1.0	1.1	0.4
						0.01—0.02	0.3—0.5	0.9—1.2		
	7	12	93.8	3.3	3.4	0.05	0.6	1.6	1.7	0.5
			78.2—97.8	0.0—21.6	0.4—9.2	0.01—0.22	0.2—1.3	0.9—3.2		
	8	8	87.63	12.32	4.5	0.06	0.5	1.3	1.4	0.4
			62.2—95.1	0.0—36.4	1.2—11.5	0.01—0.21	0.1—1.1	0.2—2.7		
	9	5	95.1	2.8	2.0	0.01	0.3	1.3	1.3	0.2
			92.6—97.1	1.0—5.4	0.9—3.9	0.01—0.02	0.3—0.5	1.1—1.8		

Continuation of Tab. 1

Rock	No. of profile	Number of samples	Calcite	Dolomite	IR	K	Th	U	Uekv.	Th/U
			weith %				ppm			
Tisovec	10	18	93.8	6.8	1.4	0.04	0.4	2.5	2.5	0.2
Limestone and			74.0—99.6	0.0—24.3	0.1—2.7	0.01—0.08	0.1—1.0	0.3—6.6		
Dolomite	11	7	8.4	91.2	0.4	0.01	0.4	0.7	0.8	0.6
			3.3—19.1	80.5—96.5	0.3—0.9	0.01—0.01	0.2—0.9	0.5—0.9		
Opponitz	12	6	85.6	9.8	8.5	0.37	1.8	0.9	2.0	2.0
Limestone			65.5—98.3	0.0—19.4	2.1—15.0	0.05—0.71	0.6—3.7	0.4—1.4		
	15	3	92.4	2.3	5.9	0.24	0.8	1.6	2.1	0.5
			88.7—95.7	0.9—5.0	2.4—6.4	0.09—0.32	0.5—1.0	0.9—2.2		
	15	1^{+}	25.5	46.8	27.9	1.85	4.0	1.9	5.4	2 1
Haupt-	15	11	5.8	92.0	2.3	0.02	0.4	1.9	2.0	0 2
dolomite			2.8—14.9	82.2—95.3	1.2—2.6	0.01—0.05	0.1—0.8	0.2—4.0		
Dachstein.	16	20	57.43	39.6	3.2	0.10	1.0	3.0	3.3	0 3
Limestone			16.9—96.4	2.0—81.2	1.1—6.2	0.01—0.28	0.3—2.4	1.8—4.1		
Reifling	18	13	93.9	—	5.9	0.19	0.9	3.1	3.5	0.3
Limestone			83.1—99.6		0.4—10.9	0.03—1.16	0.1—3.3	1.7—4.7		
Zámostie	18	2	96.6	—	3.4	0.83	2.5	3.3	5.0	0.8
Limestone			96.2—96.9		3.0—3.8	0.70—0.97	2.4—2.6	2.2—4.4		
Marly	18	2	20.1	25.5	49.4	3.33	6.6	2.3	8.4	2.9
beds			15.1—25.2	18.2—32.8	46.6—52.2	2.95—3.72	6.2—7.1	2.0—2.7		
Gutenstein	18	3	62.1	35.2	2.7	0.02	0.5	1.8	1.9	0.3
Formation			32.3—81.9	12.3—64.4	1.8—3.3	0.01—0.03	0.3—0.7	1.3—1.4		

Explanation: Profiles Nos. 1–17 in higher nappes (Veterník, Havranica, Jablonica), No. 18 – borehole DV-1 – Choč Nappe. The table shows also average values for the ratio Th/U and average summary gamma activity expressed as U_{ekv}. + – sample from the profile No. 15 with higher Fe content (Fig. 6)

DV-1 was the presence of cherts very marked. Except for them the IR values reflected also the presence of marly beds or intercalations. They were prominently represented also in the thick (approx. 200 m) formation of these limestones in the Choč Unit (borehole DV-1). The mineral composition of the IR in samples from various limestone and dolomite types did not vary considerably. The minerals determined in the IR were K-mica, quartz (small authigenic as well as clastic grains), feldspars (predominantly albite, to a lesser extent K-feldspars), chlorite, pyrite, Fe-oxides. Annaberg, Gutenstein and Reifling Limestones contained also sphalerite, less galena and celestine. In the fraction < 2 μm illite has been determined in all samples, as well as to, a lesser extent chlorite. Clay material constituted a considerable part of the IR practically in all samples.

From the ternary diagram K-Th-U (Fig. 3) where average values for different profiles have been plotted (denoted by the same numbers as on Fig. 2) it follows that the largest contribution to the bulk gamma-activity of samples with low IR is provided by U. Only profiles with higher IR (6b, 12 and 15, Fe- sample from Profile 15 with high Fe content) are shifted to the Th-apex.

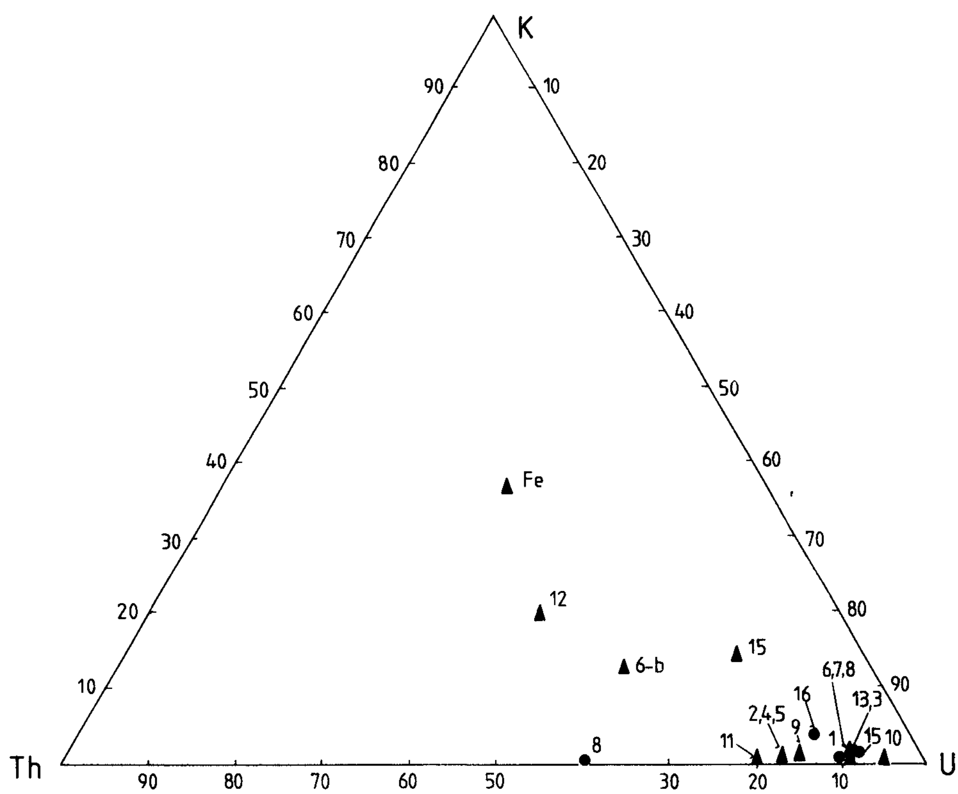

Fig. 3. K-Th-U driagram of the studied limestones (triangle) and dolomites (circle) constructed from average values on individual profiles, or several profiles of the same rock type.

Explanations: Nos. of the profiles are as on Fig. 1. See also text. Fe – one sample of Opponitz Limestone with increased Fe content.

Relationship between IR and natural radioactive element contents

We have studied the relationship between Th and IR, as well as Th and K, SiO_2, Al_2O_3, Fe_2O_3. The most marked relationship was found to be that of Th and K (Fig. 3), however, the relationship with Al_2O_3 is similar. Fig. 4 shows the correlation of Th and K for selected 56 samples with increased K or IR. They are samples from the Opponitz, Dachstein and Reifling Limestones. The contents of K as well as of Th in the rest of the samples were considerably lower and their projection points would fall into the field marked by a dashed line. The mineralogical composition of the IR allows to assume that the predominant part of K is bound in K-mica or illite. On the basis of the observed correlation between Th and K we can assume that Th is in limestone and dolomite samples bound in minerals of the IR, predominantly clay minerals.

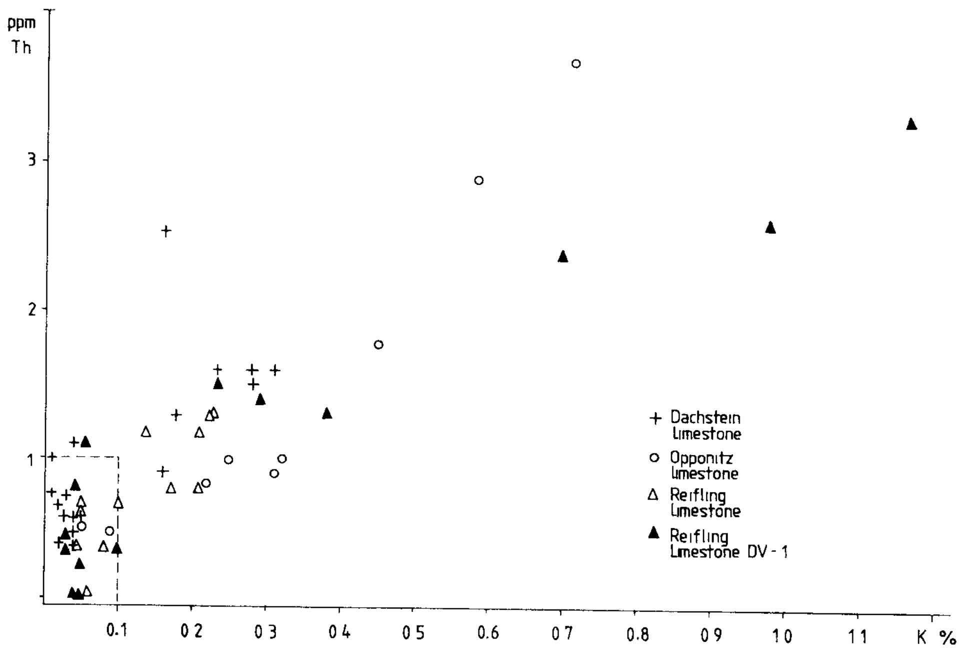

Fig. 4. Correlation between the contents of Th and K for 56 samples from sample sets (profiles) marked in the legend. These limestones had relatively increased IR. The rest of the samples (98) of limestones and dolomites with low IR would fall into the field marked on the graph by a dashed line.

The study of the relationship between U and IR, or K, Al_2O_3, Fe_2O_3, in the whole set of samples (170) did not yield any uniform positive or negative correlation trend. From Tab. 1 it can be determined that the highest values of U have been measured in limestone samples with very low IR (Profile 10). Samples of limestone with increased IR contents have comparable or lower values of U than limestones and dolomites with lower IR, even though we have determined a marked positive correlation of U and IR (relative) within these small sets. The histograms (Fig. 5) summarize the data on the distribution of U and Th concentrations for individual limestone and dolomite types.

On the basis of the obtained data we can state that a part of U is bound in the minerals of IR (e.g. clay minerals), however, it is only a small part. Already A d a m s – W e a v e r (1958) (see

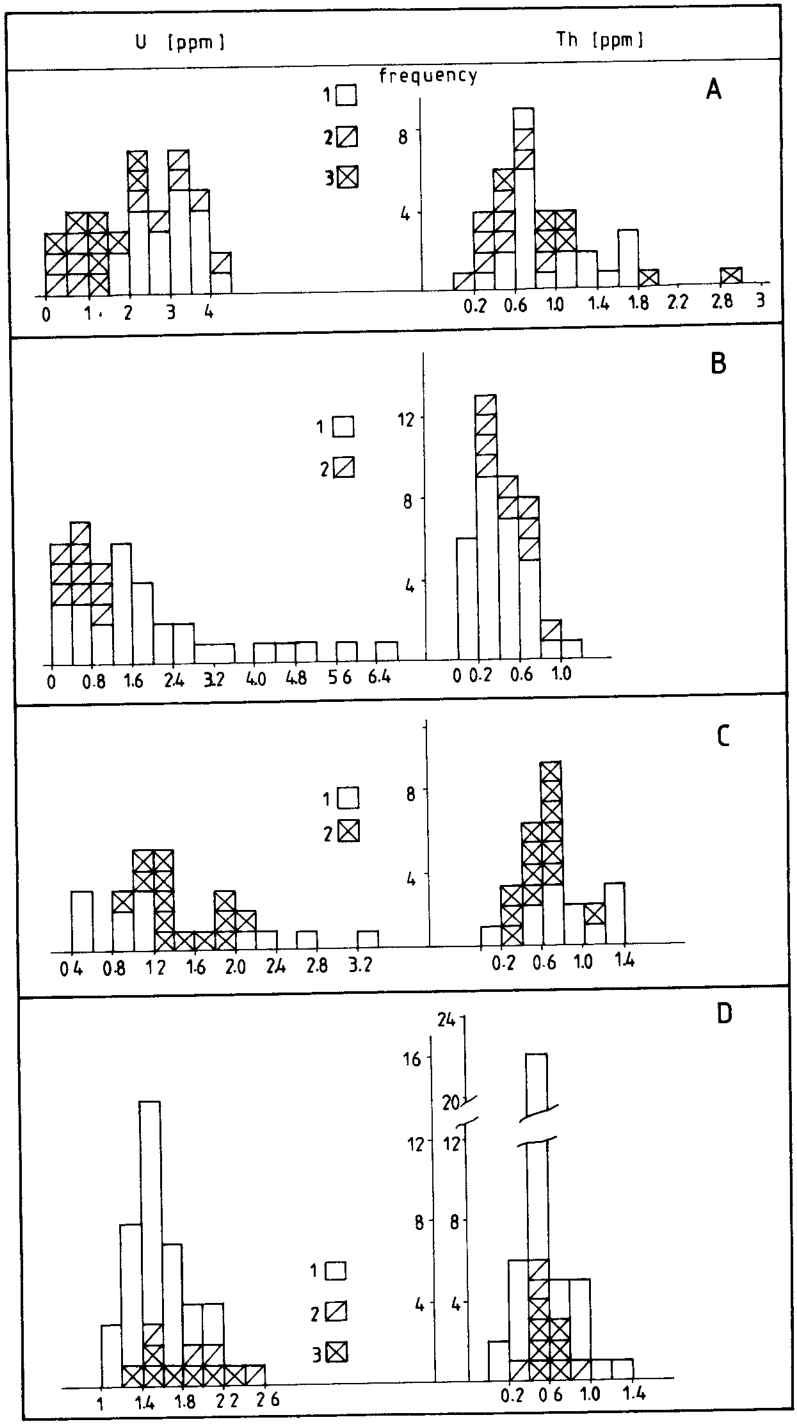

Fig. 5.

also Rodgers–Adams, 1969; Sobotovich et al., 1983) showed that approximately 80 % of U in carbonates of marine origin are bound in carbonate minerals (on their surface or in the structure) and only 20 % are associated with terrigene components (e.g. the heavy fraction, clays etc.). From the above mentioned facts it follows that the distribution of U in carbonates is controlled by more complicated processes than the distribution of Th.

Uranium contents in the distinguished facies

Middle Triassic carbonate platform facies

The following lithostratigraphic units can be classified with these facies: Gutenstein Limestone and Dolomite, Annaberg Limestone, Steinalm Limestone and Wetterstein Limestone and Dolomite.

The Gutenstein Limestone or Dolomite and the Annaberg Limestone are representing the basal members of a Triassic carbonate sequence. The Annaberg Limestone differs from the Gutenstein Limestone by its thick-bedded development, lighter colouring and more marked contents of organic detritus. The above mentioned carbonates are sediments of tidal flats and restricted lagoons of the ramp stage of carbonate platform development. The sedimentation environment was characterized by low dynamics, frequent fluctuations of salinity documented very well by the low contents and small diversity of organic remnants (crinoids, ostracods). In higher parts of the Annaberg Limestone Formation there are beds relatively richer in organic remnants, with foraminifers, dasycladaceans, globochaetas and bivalvians. This part of the formation is as far as its character is concerned similar to the Steinalm Limestones (in the profiles 5, 4) which sedimented in a more dynamic environment of the outer lagoon margin having a constant salinity. Middle Triassic Wetterstein Limestones and Dolomites represented only in the Havranica and Jablonica Units sedimented in extensive shallow-waters of the back-reef flat.

We did not observe any considerable differences in the values of U (or Th and K) among the samples of Annaberg and Gutenstein Limestones or Dolomites. The set of these carbonate types included 42 samples from profiles 1 to 5, 13 and 17 (Fig. 2) with an average content of uranium of 1.6 ± 0.6 ppm, of Th 0.5 ± 0.4 ppm (arithmetic average $\pm$ 2s). The distribution of U (Th) in a part of the formation (profiles 1 to 5) of the Veterník Nappe is presented on Fig. 6 where lithofacial and petrographic characteristics of this formation can be found as well. Gutenstein and Annaberg Limestones are predominantly dark, brownish-grey to black, weakly recrystallized micrites and microsparites with partial irregular dolomitization (Pl 1, A, B). The even and relatively narrow range of U values is a consequence of the monotonity of sedimentation in this part of the formation, with no considerable changes. It is confirmed also by the low grade of limestone recrystallization. The dolomite samples (Profile 1) display a wider range of U values; diagenetic processes probably affected considerably its distribution.

Fig. 5. Histograms for Th a U in the distinguished facial rock types.

Explanations: A – Upper Triassic shallow-water limestones and dolomites, 1 – Dachstein Limestones, 2 – Hauptdolomite, 3 – Opponitz Limestone. B – forereef and reef limestones and dolomites, 1 – Tisovec Limestone, 2 – Tisovec Dolomite. C – basin and slope limestones, 1 – Reifling Limestone, 2 – Raming Limestone. D – Middle Triassic carbonate platform facies, 1 – Annaberg Limestone, 2 – Gutenstein Limestone, 3 – Gutenstein Dolomite.

Plate 1

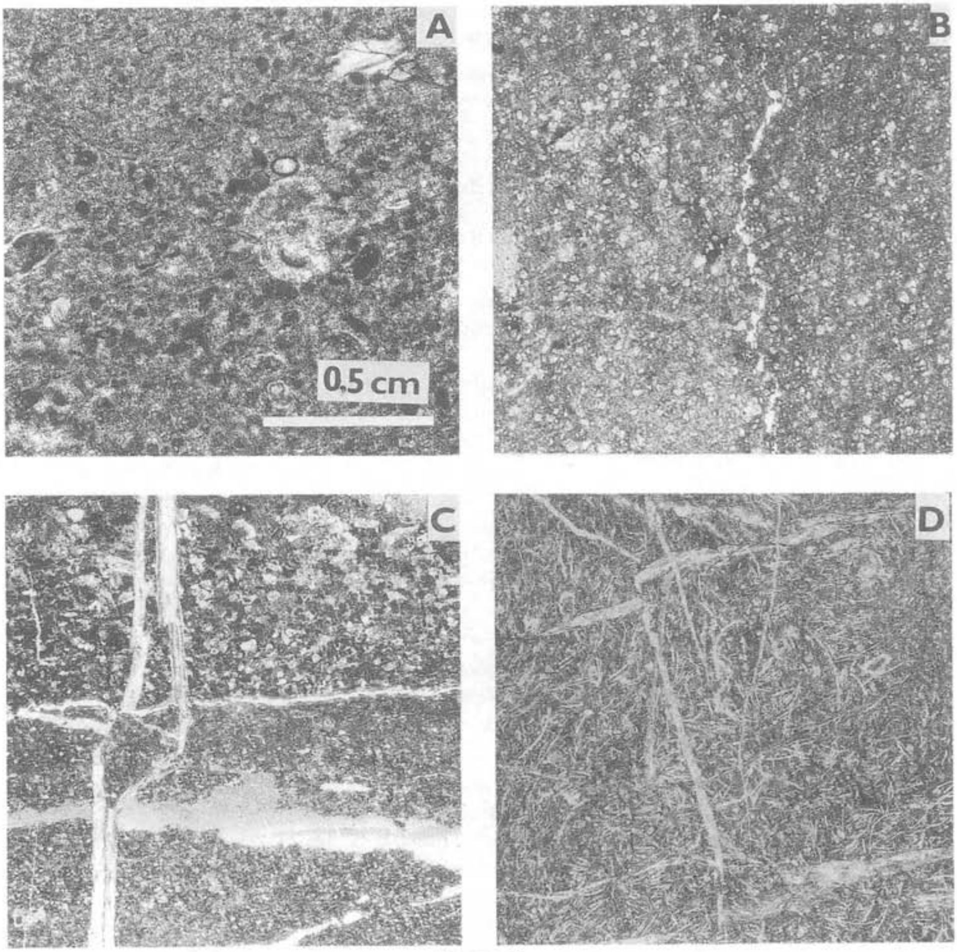

Plate 1

Fig. A. Recrystallized microsparite limestone with bioclastic texture (wackestone). Detritus is composed predominantly of intraclasts, relics of ostracods, foraminifers and of pellets. Annaberg Limestone (Pelsonian). Location: Profile MV/82, Malá Vápenná, Malé Karpaty Mts.

Fig. B. Recrystallized partially dolomitized microsparite limestone with sporadic relics of crinoids and ostracods (mudstone). Annaberg Limestone (Pelsonian). Location: Profile MV/82.

Fig. C. Gradationally bedded detrital lamina in Reifling-type limestone (wackestone-packstone) with intraclasts, bioclasts and pellets. Typical slope facies from upper parts of the Reifling Formation (Longobardian-Cordevolian). Location: Profile MAd/84, Mokrá Valley, Malé Karpaty Mts.

Fig. D. Biomicrite limestone (packstone) with typical pelagic filamentous microfacies. Except filamets there are calcified radiolarians. Basin facies of the Reifling Formation (Longobardian). Location: Borehole Dobrá Voda 1, Brezovské Karpaty Mts.

Basin and slope facies

Reifling Limestones are the product of an important Middle Triassic episode of basin and slope sedimentation. They sedimented in regions of depressions formed by subsidence of certain parts of the carbonate platform. In contrast to pelagic limestones of the open sea they are poorer in micro- as well as macrofauna. The prevailing type are biomicrite limestones with sporadic filaments and radiolarite. Relatively frequent are beds of fine-laminated, gradationally bedded limestones with flow-oriented detritus containing relics of foraminifers, globochaetas and crinoids, which indicates the proximity of the source region – the platform margin. This type of facies is typical of the upper part of the Reifling Limestone Formation in theVeterník Nappe which we consider to be slope sediments (Pl. 1, C).

Reifling Limestones of the Choč Unit determined in the borehole Dobrá Voda 1 can be considered to be relatively deeper-water sediments in comparison with the Reifling Limestones of the Veterník Nappe (Fig. 2). It is indicated by the facial diversity (clay beds, nodular cherty limestones, massive cherty limestones) (Pl. 1, D) and considerable thickness of the formation (Michalík et al., 1987). The differences are reflected also in the values of U. Reifling Limestones from the borehole DV-1 are characterized by higher U contents (in average 3.1 ± 1.8 ppm) than limestones of the Veternica Unit (profiles 6–9, in average 1.4 ± 1.2 ppm).

On Fig. 6 we can follow the changes in the contents of U (Th) in relation to the facial character of the formation. In the lower part of the Reifling Limestones consisting predominantly of dark, thick-bedded, markedly nodular sequences with cherts the values of U are uniform and similar to the values of the Annaberg Limestones. This is a case of a continuous passing (deepening) from platform facies of the Annaberg Limestones through lagoon (Zámostie Formation) to basin facies of the Reifling Limestones.

In the upper part of the Reifling Formation (Fig. 6) we can observe the opposite process – gradual continuous shallowing. This development is retained in the slope facies which pass into forereef and reef facies; this indicates a progradation of the Upper Ladinian–Lower Carnian platform. The values of U in these limestones are considerably variable.

The presence of claystone beds in the Reifling Limestone Formation (borehole DV-1) increases the bulk gamma-activity, since the contents of Th and K in them are higher (Fig. 4).

Reef and forereef facies of the Lower Carnian carbonate platform

Above the slope facies of the Reifling Limestones in the Veterník Nappe occur light limestones denoted as Veterník Limestones, parallelized later with the Wetterstein and Raming Limestones. According to the latest knowledge the above mentioned limestones are Carnian in age and they can be parallelized with the Tisovec Limestones (Masaryk, 1987).

Basal members of the large reef complex (Profile 10) are formed by megabreccia-like forereef sediments. During the Lower Carnian they represented the frontal sediments of a prograding platform which gradually filled the existing depressions where basin and slope facies of the Reifling Limestones had sedimented in the Anisian. Towards the overlying beds this lithofacies is substituted by detrital dolomitic limestones (Pl. 2, A) with beds of dark, heavy-bedded micritic limestones. In the upper parts there are already massive organogenic limestones of the reef edge containing a rich community of reef-forming organisms, predominantly calcareous sponges, algae and corals (Pl. 2, B). Towards the overlying beds the limestones are gradually interbedded by whitish-gray dolomites (Profile 11).

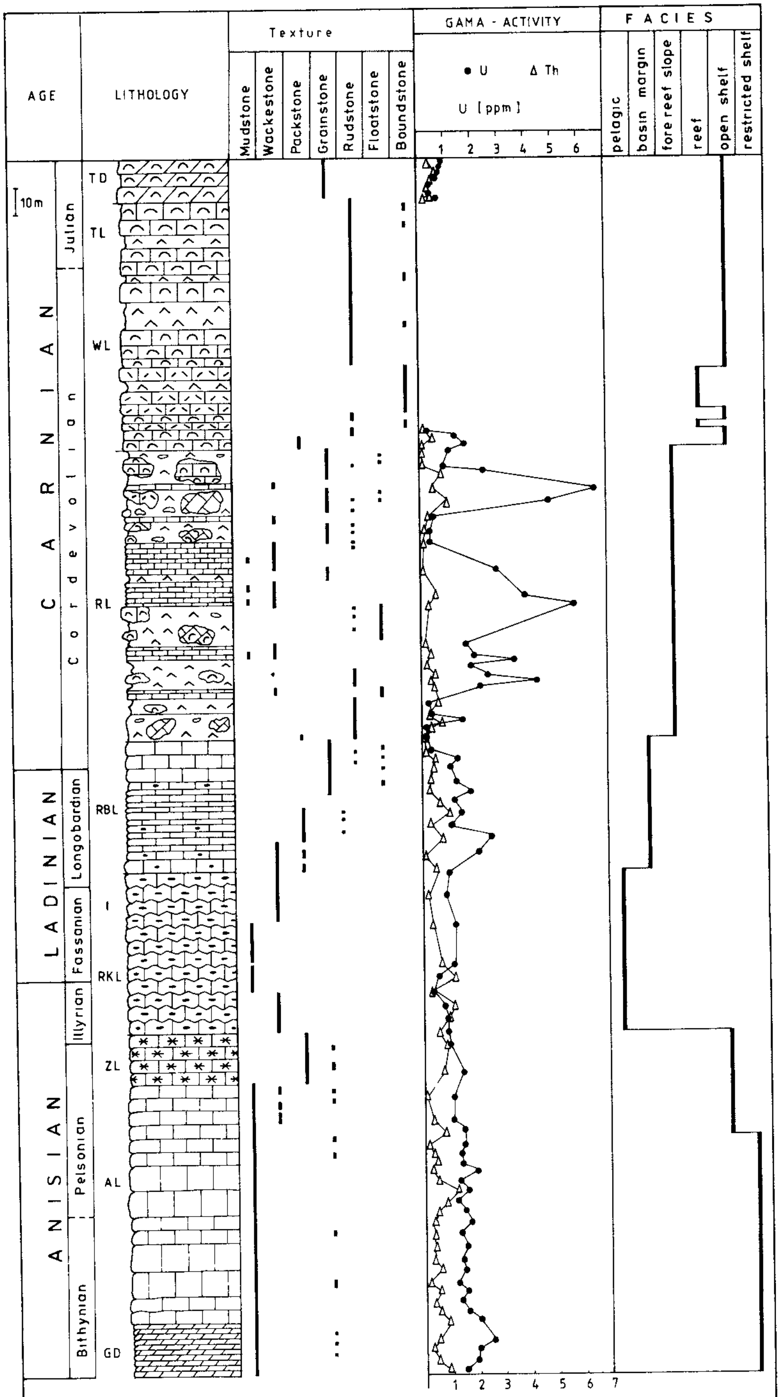
AGE
LITHOLOGY
Texture
Mudstone
Wackestone
Packstone
Grainstone
Rudstone
Floatstone
Boundstone
GAMA - ACTIVITY
• U
Δ Th
U [ppm]
1 2 3 4 5 6
F A C I E S
pelagic
basin margin
fore reef slope
reef
open shelf
restricted shelf
10m
C A R N I A N
Julian
Cordevolian
LADINIAN
Longobardian
Fassanian
ANISIAN
Illyrian
Pelsonian
Bithynian
TD
TL
WL
RL
RBL
I
RKL
ZL
AL
GD
1 2 3 4 5 6 7

Fig. 6

The lower part of the formation was not encompassed by Profile 10, but it has been studied in a quarry not far from the profile. It is formed by megabreccias composed of large blocks (1–20 m) of light-coloured reef and platform limestones in a dolomite matrix. Samples of these limestones and dolomites had low concentrations of U (0.2–1.6 ppm), however, they are similar to the values measured in light limestone blocks on the Profile 10. High U contents have been recorded in dark micrite limestones (2.2–6.6 ppm), in contrast to the values of light organogenic limestones (0.5–1.8 ppm). Uranium accumulated in dark thick-bedded limestones probably due to changes of oxidation-reduction conditions. From the development of the sedimentary environment it follows that these forereef sediments could accumulate organic matter. Fig. 7 presents a model of the development of sedimentation in the Illyrian to Karnian; the figure shows the formation of slope to forereef sediments.

In the dolomitized part of the reef complex (Profile 11) U contents decrease again and they approach the values determined in organogenic limestones (0.5–0.9 ppm). Dolomitization caused by diagenetic, probably hypersaline solutions (Fig. 7 – high Na content) could contribute to the decrease of the U content.

Facies of Upper Triassic carbonate platform

We classify with this group the Opponitz Limestones, Hauptdolomite and Dachstein Limestones.

The Opponitz Limestone (Profiles 12, 15) is represented in the Malé Karpaty Mts. region by some local occurrences on the basement of the Hauptdolomite Formation. It is a sediment of restricted lagoons with limited circulation and low dynamics of the environment. Predominant are slightly marly, sporadically lumachelle limestones with claystone intercalations. These micritic limestones with sporadic occurrences of organic detritus have generally low U contents similar to the values determined in the Annaberg Limestones. The bulk gamma-activity is increased by Th or K bound in the minerals of the IR.

The Hauptdolomite Formation are sediments of vast shallow waters of the inner and middle shelf. Dolomites lying above the Opponitz Limestones in Profile 15 can be divided on the basis of their petrographic characteristics as well as U distribution into two parts. Above the limestones there are dark, heavy-bedded dolomites with predominantly microsparite texture and frequently stromatolite beds. They have increased U contents - 2.1–3.7 ppm. The content of IR is very low, resulting in low Th and K values. Light, strongly crumbling and recrystallized, in places even brecciated dolomites in the upper part of the formation have low U contents - 0.2–0.6 ppm. On this profile we can demonstrate the distribution of uranium varying in relation to the sedimentation environment and dolomitization conditions. Carbonates with loferite cycles sedimented in the region of tidal flats having low dynamics of environment. Dolomitization took place in the early diagenetic stage of development. Light massive dolomites are the product of late-diagenetic dolomitization of middle-shelf limestones.

◄

Fig. 6. Schematized profile of the Veterník Nappe in the Malé Karpaty Mts. The scheme shows the correlation between the distribution of U and Th, sedimentary textures and sedimentation environment.

Explanations: TL – Tisovec Limestone, RL – Raming Limestone, RBL – Reifling Limestone – Bankkalk, RKL – Reifling Limestone – Knollenkalk, ZL – Zámostie Limestone, AL – Annaberg Limestone, GD – Gutenstein Dolomite.

Plate 2

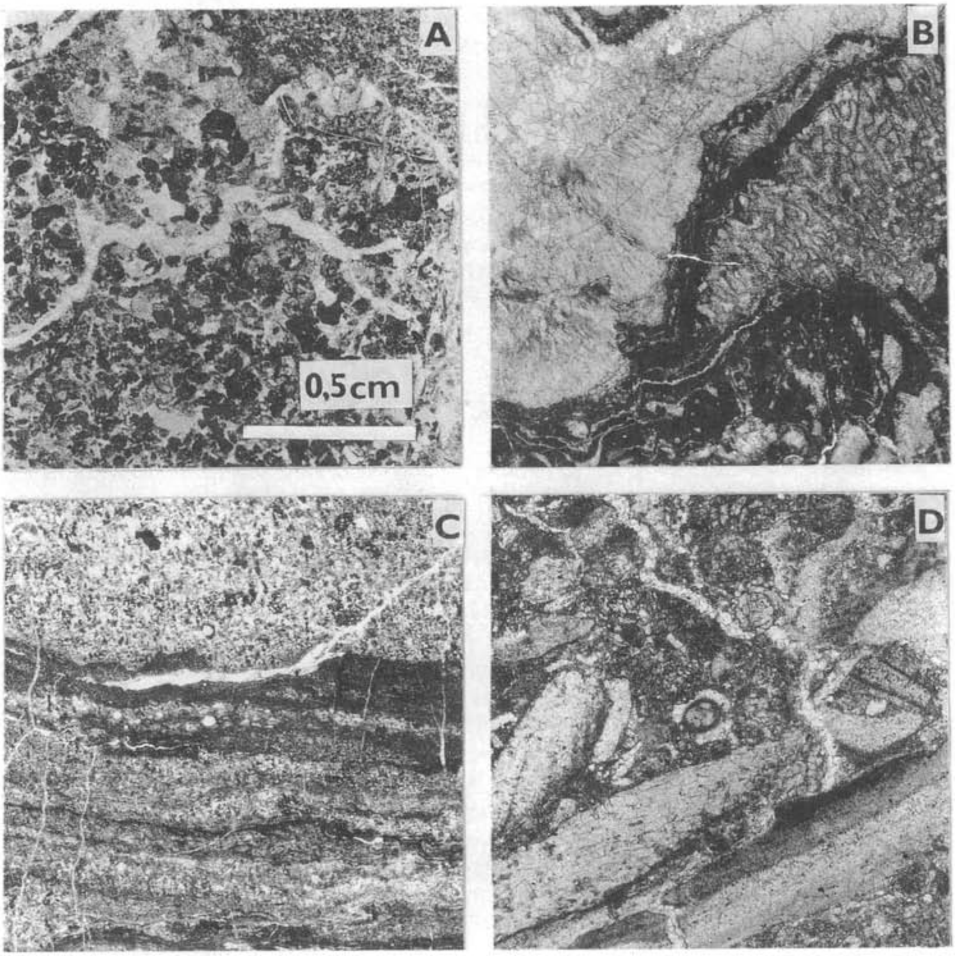

Plate 2

Fig. A. Biosparite limestone (grainstone) with micritized litho- and bioclasts, pelets and oncoliths. Slope to forereef facies in the Raming Formation (Cordevolian). Location: Profile Kršlenica, Malé Karpaty Mts.

Fig. B. Biogenic algal-bryozoan limestone (bindstone). Cavities are filled by fibrous and block calcite cement and partly also by a sediment with biosparite to biomicrosparite texture. Tisovec Limestone in reef-core facies (Cordevolian-Julian). Location: Kršlenica, Malé Karpaty Mts.

Fig. D. Coarse-detrital limestone (rudstone) with relics of bivalvians, gastropods, foraminifers and crinoids. Dachstein Formation (Sevatian). Location: Plavecký Peter II/83.

Fig. C. Stromatolite bed in detrital intrabiosparite limestone (grainstone). Dachstein Formation (Sevatian). Location: Profile Plavecký Peter II/83.

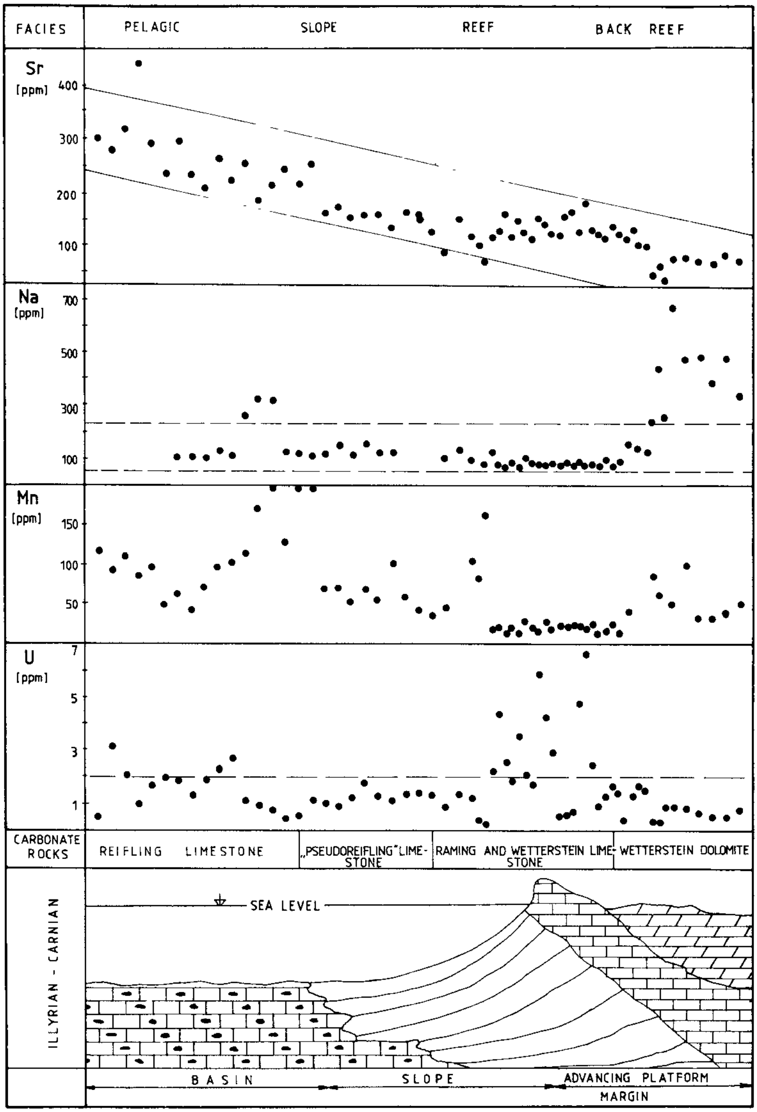

Fig. 7. Comparative graphs of the elements Sr, Na, Mn and U for a part of the Veterník Nappe Formation.

Explanations: The lower part of the figure depicts the development of sedimentation in this formation (progressing platform model, S e l l w o o d, 1986). The preexisting depressions (Illyrian) where pelagic Reifling Limestones had been formed were gradually (up to Carnian) covered by slope to reef sediments. The development of the upwards shallowing sedimentation can be well seen on the decreasing trend of Sr values, less markedly on Mn, and on the marked increase of Na contents in the back-reef dolomite formation (for more details see L i n t n e r o v á et al., 1988). The contents of U are highest in slope to forereef sediments.

The Dachstein Limestone has been studied in Profile 6, overlying the Hauptdolomite. The sedimentation environment of the Dachstein Limestones is relatively extensive, from the reef zone to the region of the back-reef lagoon. Limestones of the studied profile are mostly lagoon sediments represented by thick-bedded biomicrite limestones (Pl. 2, C). The environment of the lagoon margin is represented by high-energy biosparite limestone with abundant bivalvians and gastropods (Pl. 2, D). The inner margin of the lagoon is characterized by abundant stromatolite textures with sings of cyclicity. The contents of U in samples of the Dachstein Limestones vary in a relatively wide range (1.8–4.1 ppm) and they are relatively high. The limestones are relatively intensively dolomitized, especially in the lower part of the formation, but no direct relationship between the content of uranium and the grade of dolomitization could be determined. Samples from this part (42 to 81 % dolomite) had the highest contents of U: 3.4–4.1 ppm.

Upper Triassic limestones and dolomites which formed in the conditions of well-differentiated carbonate platform had higher contents of U and Th (K) than Middle Triassic carbonates which sedimented in an environment with less differentiated conditions – with ramp character of sedimentation. We assume that in the environment of a markedly differentiated platform uranium accumulated due to local changes of oxidation-reduction conditions. E.g. organic matter can accumulate relatively better in the conditions of lagoons (Sobotovich et al., 1983; Dongarra, 1984).

Summary

We have studied the contents and distribution of natural radioactive elements in the basic facies of Middle and Upper Triassic carbonates.

A direct correlation between the values of Th and K and the contents of IR has been confirmed. The contents of Th and K are decisive for the bulk gamma-activity of samples with high IR. In carbonates with low IR the decisive influence is that of U, while its concetrations differ in the distinguished limestone and dolomite facies. The values of U in the individual profiles vary in a relatively wide range, however, the average values cannot be considered anomalously high. The differences in U contents in the studied carbonates can be related to the primary sedimentation environment and diagenetic conditions.

The greatest differences in U concentrations (0.2–6.6 ppm) have been determined in limestones of the forereef facies, where material from different zones of carbonate shelf accumulated during the sedimentation. Different sedimentation conditions and early diagenetic alterations, as well as changes of accumulation rate in the forereef region caused the differences in U concentration in the sediments. For example, blocks of light, organogenic reef to lagoon limestones (at least partly diagenetically consolidated on the site of their origin) have lower U contents (0.2–1.8) than dark, thick-bedded limestones (2.2–6.6 ppm). These dark limestones accumulated quickly and were consolidated in the forereef zone in different oxidation-reduction conditions.

Increased U contents have been recorded also in pelagic facies (e.g. Reifling Formation of the Choč Unit: 1.7–4.7 ppm) and in Upper Triassic, predominantly lagoon limestones, or dolomites. Upper Triassic shelf limestones and dolomites have higher values of U than Middle Triassic ones. Middle Triassic carbonates formed in an environment with less differentiated conditions – ramp character of sedimentation – in comparison with the zoned and rugged Upper Triassic platform.

The cause of the change of oxidation-reduction conditions, i.e. also of the differing

U distribution in sedimentary carbonates, could thus be changes of sedimentation depth and O_2-level, the dynamics of the environment as well as the accumulation of organic matter. The study of recent sediments has shown that early-diagenetic processes most markedly affect the distribution of elements in carbonate sedimentary rocks. Diagenetic processes generally lowered the contents of U in carbonate rocks.

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REFERENCES

ADAMS, J. A. S.–WEAVER, C. E., 1958: Thorium-to uranium ratios as indicator of sedimentary processes – an example of geochemical facies. *Bull. Amer. Assoc. Petrol. Geologists* (Tulsa), 42, pp. 387.

AMIEL, A. J.–MILLER, D. S.–FRIEDMAN, G. M., 1973: Incorporation of uranium in modern corals. *Sedimentology* (Amsterdam), 20, pp. 523–528.

ALTSCHULER, Z. S.–CLARKE, R. S.–JOUNG, E. J., 1958: Geochemistry of uranium in apatite and phosphorite. *Geol. Surv. Profess. Paper* (Washington), 314-D, pp. 45–89.

BIELY, A.–BYSTRICKÝ, J.–MELLO, J., 1980: Problematika hronika a „gemerika" v Malých Karpatoch a vo Viedenskej panve. Materiály XXIII celoštátnej geologickej konferencie slovenskej geologickej spoločnosti. *GÚDŠ* (Bratislava), pp. 17–30.

DONGARRA, G., 1984: Geochemical behaviour of uranium in the supergene environment. In: De Vivo, B. – Ippolito, F. – Capaldi, G. – Simpson, P. R. (eds.) – Uranium geochemistry, mineralogy, geology, exploration and resources. *Inst. Mining and Metalurgy,* London, pp. 18–22.

FRIEDMAN, G. M., 1968: Geology and geochemistry of reefs, carbonate sediments and waters, Gulf of Aqaba (Elat), Red Sea. *J. sed. Petrology* (Tulsa), 38, pp. 895–919.

GRAF, D. L., 1960: Geochemistry of carbonate sediments and sedimentary rocks. Part III. Minor elements distribution. *Illinois State Geol. Survey* (Urbana), cir. 301, pp. 5–40.

GRIGORYEV, K. A.–ALEXEYENKO, E. D.–BARANOV, G. M.–GORTSEVSKY, A. A.–SMIRNOVA, A. D., 1975: Uranium and thorium in sedimentary rocks of the Easter Kazakhstan geosyncline-folded systems. In: Radioactive elements in the rocks: Raports of 1-st radiogeochemical congress (USSR). *Nauka,* Novosibirsk, pp. 72–76 (in Russian).

GVIRTZMAN, G.–FRIEDMAN, G. M.–MILLER, D. S., 1973: Control and distribution of uranium in coral reefs during diagenesis. *J. sed. Petrology* (Tulsa), 43, pp. 985–907.

HAGLUND, D. S.–FRIEDMAN, G. M.–MILLER, D. S., 1969: The effect of fresh water on the redistribution of uranium in carbonate sediments. *J. sed. Petrology* (Tulsa), 39, pp. 1283–1296.

LANGMUIR, D., 1978: Uranium solution-mineral equilibria at low temperatures with application to sedimentary ore deposits. *Geochim. cosmochim. Acta* (London), 42, pp. 547–569.

LINTNEROVÁ, O.–MASARYK, P.–MARTINY, E., 1988: Trace elements distribution in Triassic carbonates from the Veternik and Havranica Nappes (the Malé Karpaty Mts.). *Geol. Zbor. Geol. carpath.* (Bratislava), 39, pp. 301–322.

MANSKAYA, S. M.–DROZDOVA, T. V., 1968: Goechemistry of organic substances. *Pergamon Press,* Oxford, pp. 347.

MASARYK, P., 1987: Mikrofaciálna charakteristika triasových sekvencií vyšších príkrovov Bieleho pohoria Malých Karpát a ich korelácia s podložím Viedenskej panvy. *Miscellanea micropaleontologica* (Hodonín), II/1, 1987, pp. 153–189.

MICHALÍK, J.–BORZA, K.–BUČEK, S.–MASARYK, P.–JENDREJÁKOVÁ, O.–BYSTRICKÝ, J.–KÖHLER, E., 1986: Stratigrafia a stavba príkrovov Malých Karpát s ohľadom na vyjasnenie štruktúrnych anomalít v podloží Viedenskej panvy. Geol. Inst. of Slovak Acad. Sci., Manuscript, Bratislava, 377 pp.

MICHALÍK, J. et al., 1987: Správa o vyhodnotení výsledkov štruktúrneho vrtu Dobrá Voda 1 (Konča skaliek). Geol. Inst. of Slovak Acad. Sci., Manuscript, Bratislava, 345 pp.

MICHARD, A.–BEAUCAIRE, C.–MICHARD, G., 1987: Uranium and rare earth elements in CO_2-rich waters from Vals-les-Basins (France). *Geochim. cosmochim. Acta* (London), 51, pp. 901–910.

MO, T.–SUTTLE, A. D.–SACKETT, W. M., 1973: Uranium concentration in marine sediments. *Geochim. cosmochim. Acta* (London), 37, pp. 35–51.

ROGERS, J. J. W. – ADAMS, J. A. S., 1969: U: Abundance in comon sedimentary rocks. In: Wedepohl, K. H. (ed.) – Handbook of geochemistry II-5. *Springer-Verlag,* Berlin, sect. 92-K.

SELLWOOD, B. M., 1986: Shallow marine carbonate environments. In: Reading, H. G. (ed.) – Sedimentary environments and facies. *Blackwell Sci. Pul.,* Oxford, pp. 283–342.

SHOR, G. M.–VOROBYOV, V. P.–GIRIN, J. P., 1975: Radioactive elements in sediments of Scythian – Turonian platforms and its activated parts. In: Radioactive elements in the rocks. Raports of 1-st radiogeochemical congress (U.S.S.R). *Nauka,* Novosibirsk, pp. 45–52 (in Russian).

SMISLOV, A. A., 1975: Uranium and thorium in minerals of the Earth's crust. In: Radioactive elements in the rocks. Raports of 1-st radiogeochemical congress (U.S.S.R.). *Nauka,* Novosibirsk, pp. 10–18 (in Russian).

SOBOTOVICH, E. V.–BONDARENKO, G. N.–KOVALYUKH, N. N., 1983: Isotopic-geochemical pecularities of the sea sediments. Akad. Nauk SSSR, *Naukovaya dumka,* Kiev, 239 pp (in Russian).

STARINSKY, A.–KATZ, A.–KOLODNY, Y., 1982: The incorporation of uranium into diagenetic phosphorite. *Geochim. cosmochim. Acta* (London), 46, pp. 1365–1374.

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