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REE, U, Th AND K GEOCHEMISTRY OF THE MICA SCHISTS (THE KOHÚT CRYSTALLINE COMPLEX, THE WESTERN CARPATHIANS)

(6 Figs., 1 Tab.)



Abstract: On the basis of evaluation of REE, U, Th and K contents in the mica schists from the Kohút crystalline complex of the Western Carpathians it has been concluded that clay sediments were their protolite. Their source area was the Continental Upper Crust. Albite gneisses occurring in the association with mica schists differ in lower representation of clay fraction and higher quartz content in the protolite.

Резюме: Оценкой содержаний р. з. э., U, Th и K в слюдяных сланцах когутского кристаллического комплекса вепорикума Западных Карпат был сделан вывод, что их протолитом были глинистые осадки. Их источником была верхняя континентальная кора. Альбитовые гнейсы, встречающиеся в ассоциации с слюдяными сланцами, отличаются низшим содержанием глинистой фракции и высшим содержанием кварца в протолите.

Introduction

Flaky garnet-muscovite or garnet-muscovite-chlorite mica schists represent a typical lithofacies of the Veporicum crystalline complex. Their spatial distribution was cartographically determined for the first time in the maps on a 1 : 200 000 scale in the sixties. They occur mainly in the region spreading from Muráň to Hnúšťa in a continuous band of 25 km in length and of 3–6 km in width in the present erosion level.

The basic characteristics of mica schists were published by Zoubek (1936). He termed them “Tisovec garnet mica schists” (the term is according to the town Tisovec). These rocks were named as “mica schists of the Brezina type” by Klíneč et al. (1962). This name is used alternatively with Zoubek’s term (l.c.) till the present.

Zoubek’s concept (l.c.) of a uniform character of the pre-Upper Carboniferous Tatricum and Veporicum rock complexes accepted till the seventies took into account clayey-psammitic sediments with intercalations of rocks of different type as the original premetamorphic types.

In his vertical scheme of division of the Veporicum crystalline rock complexes, Klíneč (1966) placed the mica schists under discussion to the newly defined Hron complex occupying the lowermost position in a complex of the Veporicum rock sequences. Lately, Bezák (1988) has distinguished several main sequences in the broader area of the studied complex outcrop: a) the Kráľova hofa (granitized) complex, b) the Ostrá complex, c) the Klenovec complex, d) the Sinec complex, e) the Lovinobaňa complex, f) the Rimavica complex. Nevertheless, garnet mica schists represent a dominant rock type of the Ostrá complex. They alternate with amphibolite, graphitic metaquartzite and metacarbonate bodies.

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Stratigraphic pertinence of the mica schist complex under discussion is dealt with disunitedly in the Western Carpathian literature. Some of the authors consider them as the Hercynian-metamorphosed Lower Paleozoic sediments (Klinec – Planderová, 1979; Bezák – Planderová, 1981), the other ones consider them as the Upper Proterozoic sediments metamorphosed in 2 or 3 metamorphic cycles. Since the stratigraphic pertinence of the studied mica schists does not represent a key problem of this paper, we shall not be dealing with it further on.

Problems of the mica schists from the Kohút crystalline complex have been dealt with lately in the papers of Bezák (1989) and Hovorka – Méres (in press) where some aspects of metamorphic development and lithology of the mica schist complex are summarized.

Discrepancy or dilemma of the present information on the mica schists from the Kohút crystalline complex results from:

- a) lack of data on pre-metamorphic protolite character;
- b) disunitedly comprehended age of this complex even in spite of existing palynological data from the rocks with bituminous admixture forming intercalations in the mica schist complex;
- c) disunitedly comprehended sedimentary-metamorphic development of the rock set under study, whereby there are concepts of presence of the progressive and regressive stages of one metamorphic event and, at the same time, concepts of participation of several metamorphic events in formation of resultant mineral association;
- d) hitherto undistinguished and undetermined metamorphic-recrystallization effects of the Variscan and Alpine metamorphic cycles;
- e) disunitedly comprehended relations of the mica schist complex to the surrounding rock sequences.

Characteristics of the mica schists

Main rock type of the studied mica schist complex is represented by flaky garnet-muscovite mica schists (Fig. 1). They are characterized by distinct metamorphic foliation, whereby foliation planes are overfolded in detail. Garnets have usually a porphyroblastic development (up to 1 cm, most often 3–5 mm). Dominant mineral phase is represented by muscovites. They have heterogeneous character occurring in form of large (2–5 mm) flakes and in form of lepidoblastic aggregates of minute flakes of sericite development. Albite distribution is markedly uneven in this type of mica schists. Quartz is concentrated mostly to the flat elongated layers or to monomineral lenticles of dm–m size. Characteristic structural feature of the mica schists is their laminar fabric with alternating laminae with prevailing muscovites and laminae formed by albite and quartz. The mica schists are intensively overfolded, whereby amplitude of the folds is extremely variable (mm–m size).

In addition to the described main (and, at the same time, markedly dominant) type of the mica schists with typomorphic muscovite (sericite), the types with variable, but minor biotite representation are present in the mica schist complex. Chlorite, locally staurolite and kyanite are present in the mica schists (Hovorka – Méres, in press).

Petrographically different type in the mica schist complex is represented by fine-grained, mostly plane-schistose metasediments. In contrast to the above types, albite (though its distribution in the rock is uneven) and biotite are essentially represented in their mineral composition. The rocks under discussion have predominantly a character of fine-grained albite gneisses (Fig. 2). Bezák (1988) placed them as a principal rock lithotype to the Klenovec complex defined by him.



Fig. 1. Muscovite mica schist from the Ostrá complex folded in detail. Sample SY-17, magn. 48 x, X pol.

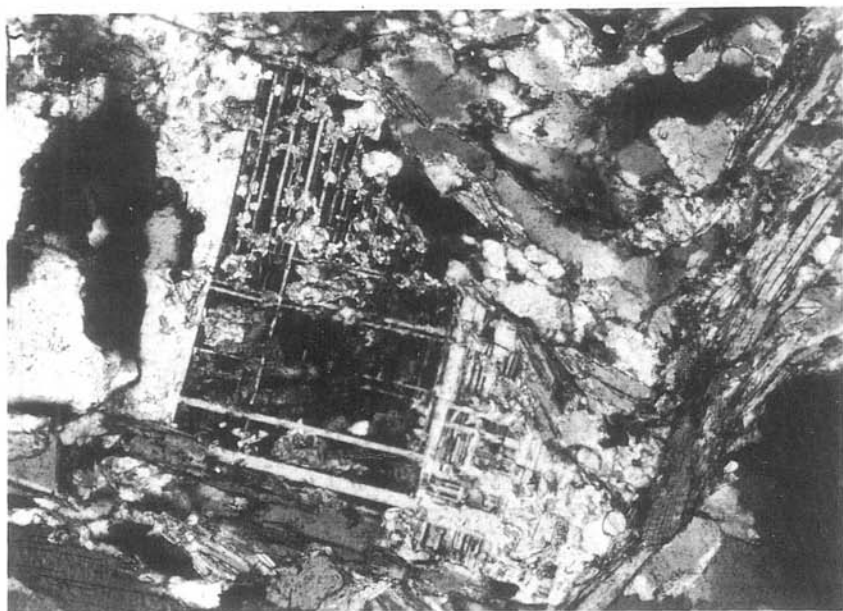


Fig. 2. Albite poikiloblast in quartz-muscovite matrix of albite gneiss from the Ostrá complex. Sample SY-2, magn. 48 x, X pol.

Geochemistry of the mica schists

Geochemical characterization is based on REE, Th, U and K determined in 5 samples of garnet-muscovite mica schists from the Ostrá complex (analyses Nos. 5, 7, 9, 15, 16) and in 3 samples of albite gneisses from this complex (analyses Nos. 2, 3, 13). The analyzed samples represent the rock types chosen from a larger set of samples after detailed microscopic study. The studied elements were determined by INAA method (Stráž pod Ralskem). The results are listed in Tab. 1.

Gneisses and mica schists are the most widespread types of metasediments in the pre-Upper Carboniferous complexes of the Central Western Carpathians. In scientific discussions, genesis and metamorphic history of gneisses and mica schists are associated in a different degree, whereby the mica schists are often considered as diaphorites of gneisses or as protolite of uniform character recrystallized under lower PT conditions. For this reason, chemical composition of the mica schists is compared with the available data on chemical composition of the gneisses from the Suchý, Malá Magura and Malá Fatra Mts. in geochemical characterization and solving of the protolite type (Hovorka – Méres, in press). The latter are regarded as representative types for the gneisses from the central zone of the Western Carpathians and hence they are denoted by G. Next comparative rock type is represented by the Muráň gneisses (MG) occurring in association with mica schists and albite gneisses, having identical or very close characteristic features (metamorphic development, mineral associations, age?; Hovorka – Méres, in press). Analytical data are taken over from Hovorka et al. (1987).

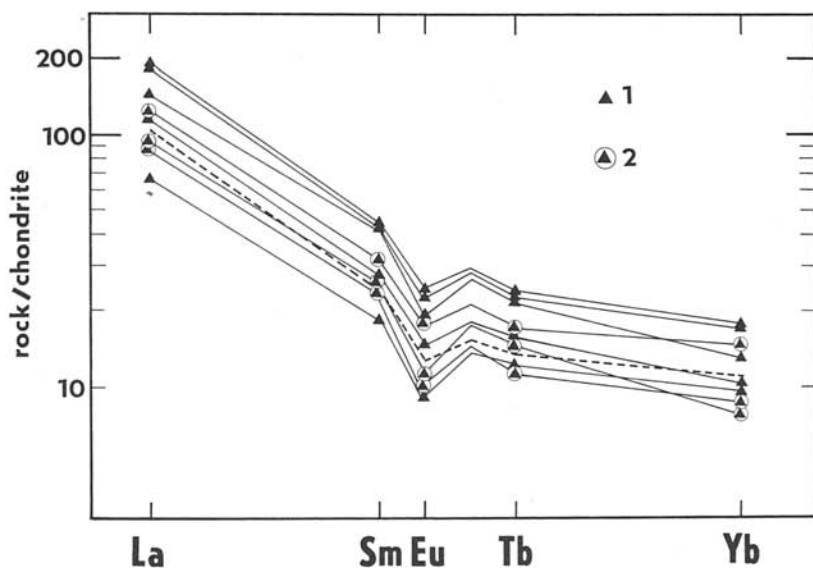


Fig. 3. REE distribution in garnet-muscovite mica schists (1) and albite gneisses (2) from the Ostrá complex.

Curves of normalized contents are parallel to PAAS (dashed) – normalized after Taylor – McLennan (1985).

Table 1

REE, Th, U and K contents in garnet-muscovite mica schists and albite gneisses from the Ostrá complex and their average values in various rock types and parts of the continental crust

	SY-2	SY-3	SY-5	SY-7	SY-9	SY-13	SY-15	SY-16	AG	MS	MG	G	PAAS	UC	TC
La	34.50	33.00	43.00	53.50	68.50	46.00	24.50	70.00	37.83	51.90	14.34	29.11	38	30	16
Ce	64.00	66.00	82.00	143.00	130.00	88.00	61.50	130.00	72.67	109.30	37.80	64.86	80	64	33
Nd	25.50	18.20	6.70	44.00	38.50	41.00	21.80	53.00	28.23	38.80	14.60	37.39	32	26	16
Sm	6.00	5.50	6.40	8.80	10.70	7.30	4.20	10.30	6.27	8.28	3.11	5.26	5.6	4.5	3.5
Eu	0.98	0.94	1.30	1.70	2.15	1.50	0.81	1.95	1.14	1.58	0.28	1.32	1.1	0.88	1.1
Tb	0.85	0.67	0.85	1.25	1.40	0.99	0.69	1.30	0.84	1.10	0.49	0.85	0.77	0.64	0.6
Yb	2.00	2.15	2.40	3.30	4.40	3.70	2.65	4.40	2.62	3.43	3.19	2.68	2.8	2.2	2.2
Σ REE	133.83	126.46	142.65	256.55	255.65	188.49	116.15	270.95	149.60	208.39	73.76	141.47	160.27	128.22	72.4
Eu/Eu ⁺	0.54	0.59	0.68	0.59	0.70	0.66	0.58	0.63	0.60	0.64	0.61	0.76	0.66	0.65	0.98
La _N /Yb _N	11.60	10.30	12.10	10.90	10.50	8.40	6.20	10.80	9.72	10.24	3.44	7.60	9.2	9.21	4.9
Th	10.70	11.40	14.60	15.50	21.80	12.60	17.80	18.30	11.57	17.60	10.54	7.81	14.6	10.7	3.5
U	3.20	3.20	2.85	2.90	3.10	2.60	3.50	2.10	3.00	2.89	2.98	2.33	3.1	2.8	0.9
K (%)	2.52	2.74	2.99	3.60	3.50	2.87	4.00	3.95	2.71	3.61	1.43	1.99	3.07	2.82	0.91
Th/U	3.34	3.56	5.12	5.34	7.03	4.85	5.08	8.71	3.86	6.09	3.54	3.35	4.71	3.82	3.85
Th/K.1000	4.24	4.27	4.88	4.31	6.23	4.39	4.45	4.63	4.27	4.87	7.37	3.92	4.76	3.79	3.85
La/Th	3.22	2.89	2.94	3.45	3.14	3.65	1.38	3.82	3.27	2.95	1.36	3.73	2.60	2.80	4.57
La/K.1000	13.69	12.04	14.38	14.86	19.57	16.02	6.13	17.72	13.96	14.37	14.56	14.63	12.38	10.64	17.58

Elements were determined by instrumental neutron activation analysis (INAA) — Stráž pod Ralskem). *Explanation:* SY — determination of analyzed sample; AG — albite gneisses; MS — mica schists; MG — Muráň gneisses; G — gneisses of the central zone; PAAS — post-Archean Australian shales; UC — Upper Crust; TC — Total Crust; K in weight %, others in ppm.

Localization of analyzed samples: SY-2: albite gneiss, outcrop in brook cut 5 km SW of Muráň; SY-3: albite gneiss, 4 km NE of Tisovec; SY-5: garnet-muscovite mica schist, 1 km N of elev. point Tri kopce (elev. point 963 m a.s.l., 6 km SSW of Muráň); SY-7: garnet-muscovite mica schist, 5 km NE of Tisovec; SY-9: garnet-muscovite mica schist, 5 km SW of Muráň; SY-13: albite gneiss, forest road cut between Rimavská Pila and elev. point Trstie (1121 m a.s.l., elev. 700 m a.s.l.); SY-15: garnet-muscovite mica schist, valley of Losinec brook, 5 km E of Tisovec; SY-16: garnet-muscovite mica schist, railway cut 0.5 km N of Hačava.

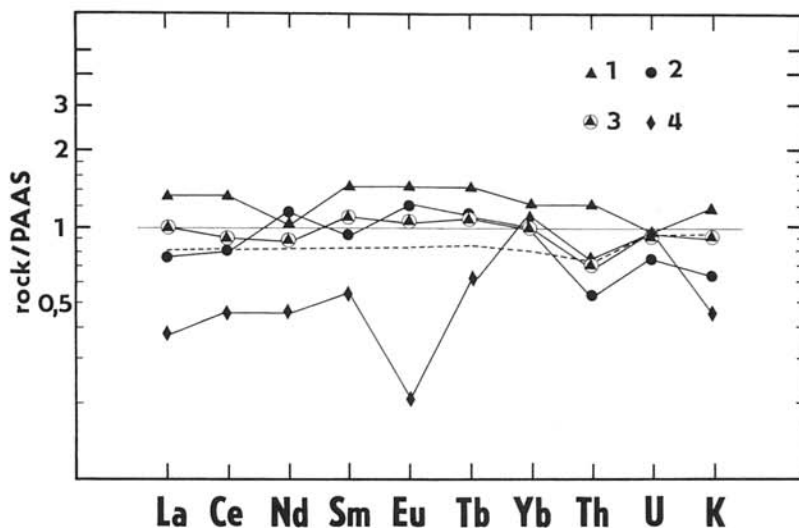


Fig. 4. Average REE, Th, U and K contents in garnet-muscovite mica schists (1) and albite gneisses (3) from the Ostrá complex, in gneisses from the central zone of the Western Carpathians (2) and Muráň orthogneisses (4) normalized to PAAS.

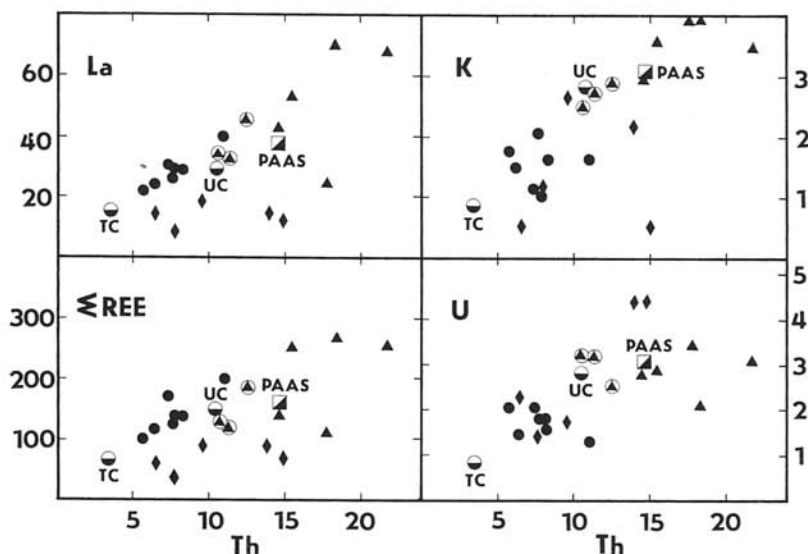


Fig. 5. Diagram of La, K, Σ REE and U: Th relations.

Explanation: UC – Upper Crust, TC – Total Crust, PAAS – post-Archean Australian shales (UC, TC and PAAS after Taylor – McLennan, 1985). Other symbols as in Fig. 4.

Further comparative analytical data are used in the paper: average values of the studied elements in post-Archean Australian shales (PAAS), average composition of the Upper Crust (UC) and average composition of the Total Crust (TC) according to the data of Taylor-McLennan (1985).

REE contents in the mica schists are typical by high REE sum which is in some cases even by 100 % higher than in albite gneisses and gneisses from the central zone of the Western Carpathians.

Course of the curves of normalized REE contents in mica schists and albite gneisses is parallel to the course of PAAS (Fig. 3); the only difference is in REE sum. All mica schist and albite gneiss samples have a negative Eu anomaly whose Eu/Eu^+ values vary from 0.54 to 0.70. Quite high La_N/Yb_N values in majority of the samples refer to their relative enrichment with LREE. From the curves of normalized average REE, Th, U and K contents in the studied rock types and in compared types (G, MG) to PAAS it follows that besides U, mica schists are largely enriched with all other elements in contrast to UC and PAAS. Besides the lower Th values, albite gneisses have very close values to those of PAAS as far as all other elements are concerned (Fig. 4).

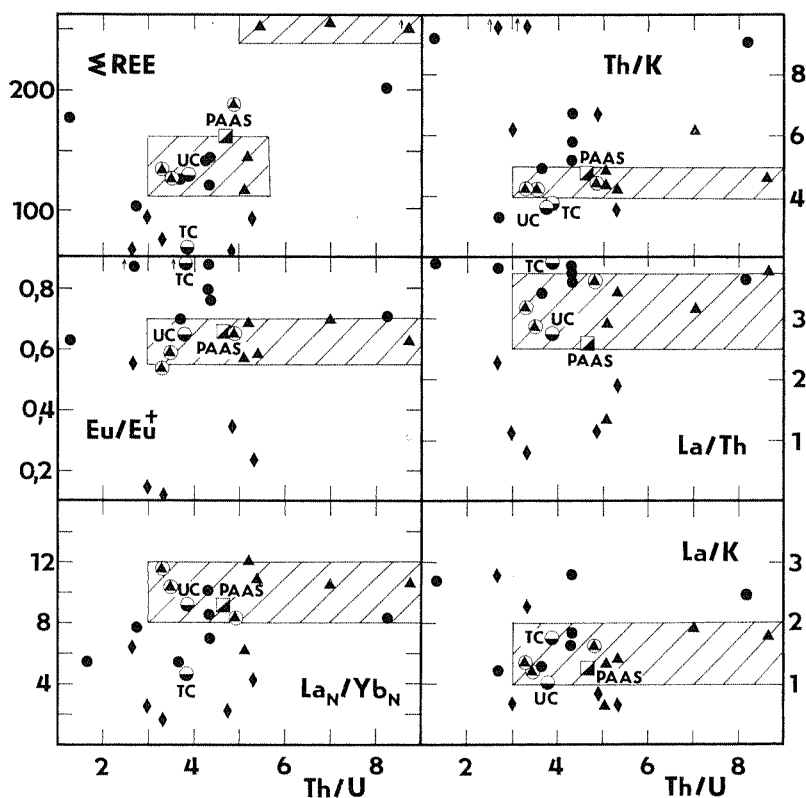


Fig. 6. Diagram of ΣREE , Th/K , Eu/Eu^+ , La/Th , La_N/Yb_N and La/K : Th/U relations. For symbols see Fig. 5. Dashed field – area of projections of garnet-muscovite mica schists and albite gneisses analyses from the Ostrá complex.

U contents in the mica schists and albite gneisses have relatively small range (Tab. 1, Fig. 5). Th contents in the albite gneisses vary within a narrow interval too when compared with the mica schists where they vary from 14 to 22 ppm. In contrast to the other compared rock types, Th/U ratio increase refers to a relative enrichment with Th in the mica schists (Tab. 1, Fig. 5). Mutual Th and K relation in the albite gneisses and mica schists is characterized by a positive correlation. The similar case is in Th and La (Fig. 5). From the relation of Th to REE sum it follows that projections of the mica schists are concentrated in two areas (Fig. 5). The first one is typical by high Th contents and REE sum and the second one is typical by relatively lower REE sum values at quite high Th contents. In comparison with the mica schists, the albite gneisses have lower Th contents and REE sum.

Most of the studied geochemical parameters (Tab. 1, Fig. 4) of the mica schists is comparable with UC and PAAS when normalization to PAAS has been done. In majority of cases, the albite gneisses occupy a position between the projections of MS and G (Fig. 4), excluding Eu/Eu^+ , La_N/Yb_N , La/K , La/Th and Th/K which are similar in the mica schists and albite gneisses displaying a smaller interval than in the other compared rock types (Fig. 6).

Discussion

REE have a specific importance in solving the protolite type of metamorphic rocks. REE are generally regarded as intact to chemical changes during diagenesis and metamorphism (Chaundhuri – Cullers, 1979; Muecke et al., 1979; Jakeš, 1984). Changes in REE distribution have been proved in some specific cases, particularly at very high rock/water ratio, but they are not caused by a constant and systematic factor. REE movement (leaching) was established, for example, in palagonitization of basaltic glass (Staudigel – Hart, 1983), as well as in spilitization (Floyd, 1977; Hellman – Henderson, 1977). On the other hand, experiments with tholeiitic glass under the hydrothermal conditions have referred to the fact that REE are immobile even in the case when the basalt is totally altered to the clay (Hajash, 1984).

Identical or comparable geochemical characteristics resulting from REE in shales from the various regions of the world (NASC – Haskin et al., 1966; ES – Haskin – Haskin, 1966; PAAS – Taylor – McLennan, 1985) and in recent clastic river sediments (Martin – Meybeck, 1979) refer to the fact that the typical shales reflect chemical composition of uncovered part of the continental crust. In majority of cases, the curves of normalized REE contents in clay sediments and sandstones are parallel to PAAS. Sandstones differ from the shales in lower REE sum (Nance – Taylor, 1976; Haskin et al., 1968). From the results of the study it follows that major REE mass in clastic sediments is bound to clay fraction and fraction below $2\ \mu\text{m}$ (Cullers et al., 1979; Chaundhuri – Cullers, 1979). In coarser, sandy fraction, there is generally lower REE sum and lower La_N/Yb_N ratio resulting from heavy minerals representation. Eu anomaly has a same character in the both fractions. REE curves in the fine-grained sediments are, in general, parallel to the UC curve, but REE sum is usually higher in them (Taylor – McLennan, 1981).

In addition to clay and grain-size fractions, the REE sum is markedly influenced by quantitative representation of quartz. Its increase is accompanied with REE sum decrease, whereby the normalized pattern is parallel to the PAAS one.

The significant parameter in REE distribution study is Eu anomaly. The fact that all post-Archean sedimentary rocks have a negative Eu anomaly (Taylor – McLennan, 1985) is important for the genetic conclusions. The only type of the sedimentary rocks where

Eu minimum has not been established is represented by some volcanogenic-sedimentary rocks formed in island arcs to the detriment of andesites, inheriting their geochemical features (Nance – Taylor, 1977). The only logical reason of Eu minimum presence in the sedimentary rocks and, accordingly, in the Upper Crust seems to be its formation during chemical fractionation in the continental crust throughout formation of K-granites which are typical by high negative Eu anomaly (Taylor – McLennan, 1985).

From geochemical characterization of the mica schists and albite gneisses from the Ostrá complex it follows that the vast majority of geochemical data is identical or comparable with these data in the shales. Projection points of the analyzed mica schist samples are projected to the close surrounding of the PAAS projection (Figs. 5, 6). In majority of cases, the albite gneisses occupy a position between the mica schists and G, they are usually situated in a close proximity of the Upper Crust average composition projection (UC). Differences between the albite gneisses and mica schists are mainly in higher REE sum and Th contents in the mica schists and, at small changes of U contents, also in higher Th/U ratio and its greater dispersion in the mica schists. Owing to the fact that K, U and Th are considered as mobile only under the high grade metamorphic conditions (Lambert – Heider, 1968; Heier, 1973), their contents in mica schists are comparable with the contents in protolite. Consequently, protolite of the mica schists was relatively enriched with Th in contrast to U in protolite of the albite gneisses. Th/U ratio is usually regarded as an important indicator of the sedimentary environment (Adams – Weaver, 1958). During sedimentogenesis, Th/U ratio varies from 0.02 to 21 due to specific behaviour of Th and U. High Th/U ratio (over 7) is characteristic of continental sediments deposited in oxide environment. In some samples of the studied mica schists, values of this ratio are close to the above value (Tab. 1). Regarding the close geochemical features, La and Th show very high positive correlation in fine-grained sediments (McLennan et al., 1980). Distinct positive correlation between La and Th in the mica schists, albite gneisses and G gives evidence for sedimentary protolite in the compared metamorphic rocks (Fig. 5). Difference is, however, in character of the sedimentary protolite. Immature (graywacke) clastic sediments prevail in protolite of the gneisses (G) (Hovorka, 1975; Hovorka – Méres, in press) what is manifested in the case of La and Th by their low values. It is supported also by a relatively low REE sum, as well as by lower K values in the Western Carpathian gneisses.

On the basis of geochemical characteristics using REE, Th, U and K, protolite of the mica schists had a character of typical clay sediments. High K, Th and La values, their mutual positive correlation (Fig. 5) and relatively most constant ratios (Fig. 6) refer to prevalence of fine-grained fraction (below 2 μm) in protolite of the mica schists in contrast to protolite of the albite gneisses. In some cases, REE sum may be influenced also by quartz content in the protolite. Eu/Eu^+ and $\text{La}_\text{N}/\text{Yb}_\text{N}$ values are very important from the point of view of the protolite rock type and a character of the source area. These values are comparable in the mica schists and albite gneisses and they are comparable with PAAS and UC data as well (Tab. 1, Fig. 6). Eu/Eu^+ values in the mica schists and albite gneisses refer to the fact that the Upper Crust where acid magmatic rocks prevailed was a source area of their protolite. Average Eu/Eu^+ value in G supports a different character of their protolite and refers to prevalence of intermediate to acid rocks of granodiorite-tonalite composition in the source area represented by the continental crust. Such relation may be caused also by higher content of basic volcanics and their clastics in graywacke protolite of the gneisses (Hovorka – Méres, in press). Eu/Eu^+ and $\text{La}_\text{N}/\text{Yb}_\text{N}$ values in the albite gneisses and mica schists refer to the same protolite type and the same source area where the Upper Crust was formed. Geochemical diversities between the mica schists and albite gneisses (higher REE sum, Th, K, Th/U contents in the mica schists) are caused by higher representation of fine-grained clay fraction (below 2 μm) in

the protolite of the mica schists than in the protolite of the albite gneisses and by higher quartz content in the protolite of the albite gneisses.

Geochemical characteristics of the Muráň gneisses are in the most of cases markedly different from the mica schists, albite gneisses and gneisses from the central zone of the Western Carpathians. Their protolite, acid magmatites took probably part in composition of the mica schists and albite gneisses protolite, but to such small extent that they did not affect essentially their geochemical characteristics.

Conclusions

The following geochemical characteristics are important for determination of protolite of the garnet-muscovite mica schists and albite gneisses from the Ostrá complex of the Kohút crystalline complex on the basis of REE, U, Th and K contents evaluation:

- mica schists have high REE sum, in some cases even by 100 % higher than in the albite gneisses and gneisses from the central zone,
- REE pattern in the mica schists and albite gneisses parallel to PAAS,
- negative Eu anomaly whose value is comparable with that in the mica schists and albite gneisses, it is lower than in the gneisses from the central zone,
- high La_N/Yb_N value in the mica schists and albite gneisses when compared with the gneisses from the central zone reaching the values typical of clay sediments,
- higher REE, Th and K values in the mica schists and albite gneisses when compared with PAAS,
- higher Th/U ratio in the mica schists when compared with the other mentioned rock types,
- positive Th and K, Th and La correlations in the albite gneisses and mica schists.

The established geochemical characteristics prove that:

- a) protolite of the mica schists and albite gneisses was represented by clay sediments (shales) whose source area was the Continental Upper Crust with prevalence of acid magmatic rocks;
- b) difference in protolite of the mica schists and albite gneisses reflected in geochemical characteristics is caused by higher representation of clay fraction and lower quartz content in protolite of the mica schists than in the albite gneisses;
- c) diversity of protolite of the gneisses from the central zone of the Western Carpathians from the studied mica schists and albite gneisses from the Ostrá complex lies not only in different grade of metamorphic recrystallization, but also in character of the protolite. Protolite of the gneisses was represented by clastic sediments of graywacke type where intermediate to basic magmatites were largely represented.

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