KYANITE-MAGNESIAN CHLORITE SCHIST AND ITS PETROGENETIC SIGNIFICANCE (THE SINEC MASSIF, SOUTHERN VEPORIC UNIT, WESTERN CARPATHIANS)

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Abstract: The Alpine metamorphic assemblage Mg-chlorite (Al-sheridanite)-kyanite-tourmaline (dravite) \pm quartz, muscovite was formed by transformation of an aluminosilicate rock (probably granite) during the process of Mg-metasomatism. The kyanite—a mineral of scarce occurrence within the crystalline rocks of the Veporic Unit, formed in an Al-Mg saturated system. The development of mineral assemblage presumed to occur at 350–420 °C under lower to medium pressure conditions (approx. 2.3-4 kb), has been prompted by the effects of allochemical metasomatism, bound spatially to the steatitization and hydrolysis of magnesite. The whole rock and mineral geochemistry indicates an increase in contents of Mg, Al, H₂O, P, Fe, Li, Ga, LREE and decrease in Si, Na, K, Ca, Rb, Ba and HREE. The tectonized and hydrothermally altered zone, characterized by occurrence of kyanite, formed during Alpine reactivation of the Veporic basement. Possible reasons to explain the lower degree of the Mesozoic cover metamorphism as well as remarkable affinity of some of the overlying Gemeric Carboniferous metamorphosed rocks to the investigated metamorphic assemblage are discussed.

Key words: Alpine metamorphism, Western Carpathians, Veporic basement, element mobility, Mg-metasomatism, leucophyllite, kyanite-Mg-chlorite-dravite assemblage.

Introduction

This paper addresses mostly to the easily weathered pale rock with macroscopically visible kyanite, which crops out in the Sinec Massif near Hnúšťa (see Fig. 1B) within the southern Veporic basement. This occurrence had already been reported by Kužvart (1955), but no genetic or age characteristics were suggested.

In the Eastern Alpine region, the quartzites with Mg-chlorite (so-called leuchtenbergite) ±kyanite were already studied in petrographic terms by Vendel (1933). The origin of these rocks has been envisaged as either sedimentary, as a result of metamorphic overprinting of clayey, (predominantly kaolinic) sandstones (Wieseneder 1968; Flugel & Neubauer 1984), altered volcanics (Lelkes-Felvári et al. 1982), or sometimes evaporites (Schreyer & Abraham 1977; Jarousse et al. 1978). Other concepts refer to these rocks as metasomatic products of gneiss alteration (Vendel 1933; Friedrich 1947; Exner 1964; Moditatedi & Wieseneder 1974; Moine et al. 1989). In the second case, the kyanite-leuchtenbergite quartzites associate with sericitic (muscovitic) or Mg-chloritic quartzose phyllites, which are products of a tectonic deformation and material exchange within the gneiss-granitic series. The above summary suggests, that we are really dealing with several possible derivation paths of these rocks.

"Glittering white schists with yellowish, or greenish tints" were recognized by Čížek on the geological map as early as 1854. Due to their fine-grained scaly and schistose texture, the rock has been labelled leucophyllite (Starkl 1883), and the increased contents of MgO in comparison to the common sur-

rounding rock has been emphasized. The leucophyllites, also called white schists etc. (Weisstein, Weisschiefer, Kornstein) associate quite often with talc-chlorite deposits and are frequently located within Hercynian metamorphic complexes. The age of these deposits, and of the leucophyllites as well, is placed in the Eastern Alps into the Alpine period (Friedrich 1968; Modjtehedi & Weiseneder 1974), which is well evidenced by both structural and geochronological data. On the other hand the chloritic-talc deposits of the French Pyrenees formed, in the course of the late Variscan tectono-deformational process (Fortune et al. 1980 in Moine et al. 1989).

Geological setting and mineralization

The Western Carpathians Mts. (Fig. 1A) form the northern branch of the Alpine-Carpathian system. Widely accepted classification divides the Western Carpathians into three major units: the Outer Zone (Flysch Belt), the Pieniny Klippen Belt and the Inner (or syn. Central) Zone (e.g. Andrusov 1968; Biely 1989). In respect to the Mesozoic cover sequences the basement is divided into Tatric and Veporic Units, which represent together with the Gemeric and Mesozoic nappes (s.c. Fatric and Hronic Units), the Central Western Carpathians. Its essential formation was completed during the pre-Senonian northward shortening. The existence of a particular relation between the southern and the northern Veporic Unit has been demonstrated by the different stratigraphic record of the cover sequence and partly also by a slighty stronger tectono-metamorphic reworking of the Southern part (e.g. Biely & Fusán 1967; Andrusov 1968).



Fig. 1A. The Slovak territory of the Western Carpathians Mts., arrow locate the studied area depicted in Fig. 1B.

Recent geological research on the Sinec Massif (Fig. 1B) has been carried out mainly in connection with prospecting of the surroundings of the local occurrence of talc-magnesite ores. Due to the lithological diversity and ambiguity in interpreting the origin of tectono-deformationally and hydrothermally affected rocks, the concepts of the geological structure also differ.

Magnesite-talc bodies are located mostly within the sericitic-chloritic host rock. This implies a concept of a wider occurrence of low grade metamorphic complex within the rock inventory of the Sinec Massif (Redlich 1934; Šuf 1937; Bezák 1988). The low grade metasediments represent an upper structural horizon and its stratigraphic age is probably Upper Carboniferous (Bezák l.c.). The second interpretation demands that these rocks belonging to the Veporic crystalline rocks, affected by deformational and metasomatic processes (Kužvart 1955; Lisý 1971; Vitásek 1989 and also Šuf 1937 if the host rock of the talc-magnesite lenses be considered).

Kužvart (1955) questions the presence of porphyroids determined by Šuf (1937) and postulates instead their being mylonitized and locally recrystallized granitoids. More intense mylonitization of granitoids and biotitic gneisses (Fig. 1) results in their transition to form chloritic-sericitic schists. This author observed gradual transitions from chloritic-sericitic through chloritic (clinochlore) up to clinochlore-talcose schists, which are found at the immediate contacts with the steatitized magnesite body. Besides this occurrence Kužvart (1960) also mentions other significant occurrences of sericitic phyllonites and leucophyllites in the wider region, spatially bound to granitoids.

A dislocation zone separating the paragneisses from the southern granitoid-migmatite zone (Fig. 1), in which the magnesite-talc bodies are located (however they do not crop out at the surface), formed probably during the Hercynian period, but it was reactivated during the Alpine Orogeny (Kužvart 1955). The thickness of this zone is variable - ranging from nearly imperceptible signs up to hundreds of meters, nevertheless, it is usually not a simple task to decide, whether the investigated rock should be interpreted as a product of a deformed basement rock, or remnants of the in-folded low metamorphosed complex. The U/Pb method on zircons dates the Sinec granites to 350 Ma (Bibikova et al. 1988). Extensive deformation of rocks as well as steatitization are assumed to be Alpine processes (Kužvart 1955; Abonyi & Abonyiová 1981). The origin of the West-Carpathian magnesites remains a lasting and unsettled problem, however, the majority of workers accept the concept of hydrothermal-infiltrational alteration of initially calcitic-dolomitic carbonates. Absence of paleontological data, differences in position, lithological and metamorphic features of present Mg-carbonates, compared to the Gemeric Carboniferous, results in their being allocated to the so called Veporic type, representing a synsedimentary component of the metamorphosed crystalline complex (Kužvart l.q., Abonyi & Abonyiová l.q.).

In contrast to these unresolved problems, a reasonable consensus has been reached concerning the origin of talc deposits. Most of talc had formed on account of magnesite due to infiltration of fluids enriched in SiO_2 (Čech 1951; Kužvart 1955) and this reaction (s.c. steatitization) can be expressed by following formula (Redlich & Cornu 1908):



Fig. 1B. Geological sketch map of the studied area (Kuthan et al. 1963). Circle with numbers shows sites of sample collection at within the tectonic zone between paragneisses and migmatite-granitoide complex. Numbers refer to rock samples in Tab. 4.

$$3 \text{ MgCO}_3 + 4 \text{ SiO}_2 + \text{H}_2\text{O} = \text{Mg}_3 \text{Si}_4 \text{O}_{10}(\text{OH})_2 + 3 \text{CO}_2$$
 (1)

The best quality talc forms at the margins of more intensely tectonized magnesite bodies, which are favourable for enhancing the mass transfer (Derco 1986). Sample location is shown on the geological sketch map (Fig. 1), constructed in accordance with the concept of strong Alpine diapthoresis of the crystalline rocks (Kuthan et al. 1963).

Methods

Original rock sample, weighting some 5 kg, has been split and pieces weighing 2-3 kg were submitted for geochemical analysis. Silicate analysis, using RFA method, has been made in the GP laboratory Spišská Nová Ves, trace elements were analysed using spectral methods — mostly ICP and the AAS was used in some cases (Tab. 4b). The INAA method, carried out in the laboratories in Černošice near Prague, was applied (Tab. 4c) to analyse REE and Rb.

The scanning electron microscope JSM-840 installed at the D. Štúr Institute of Geology has been applied to study the differences in composition of Mg-chlorite phases. The scanning images were produced under accelerating voltage 25 kV by the average intensity 10^{-9} A. These operating conditions warrant reasonably good resolution even in cases of very small differences in atomic weights (0.X-2 %) of individual phases (e.g. Fig. 7).

Mineral composition was analysed using the Jeol Superprobe 733, working under standard conditions (15 kV, 2.10^{-6} A and the electron beam diameter 3 µm) in the laboratory of elecron microanalysis run by the operating team of the D. Štúr Institute of Geology. In calculating the structural formulas all the iron was calculated as bivalent. The following numbers of oxygens were taken into calculations: chlorite 28, muscovite 22 and tourmaline 24.5. The stoichiometric formula for tourmaline has 31 oxygens, however, subtracting 3 atoms B (corresponding to 4.5 oxygens), which occur frequently in the triangular coordination (Tsang & Ghose 1973 in Henry & Guidotti 1985) and four hydroxyl groups (i.e. 2 oxygens) the above value results.

Petrologic observations

Mineral composition, observed in thin sections prepared from rocks cropping out at the locality No. 1 (Fig. 1), is characterized by the predomination of Mg-chlorite (70-95 vol. %) over muscovite, quartz, kyanite, tourmaline and accessory minerals. Phenocrysts of kyanite are distributed irregularly within the lepidoblastic (locally granolepidoblastic) matrix. Cross-cutting secondary cleavage (s₃) deforming the mineral assemblages in brittle regime has been also observed. These deformation structures locally resemble the extensional structures of shear-band type. The s2 planes, delineated by extensions of Mg-chlorite grains are considered to be the penetrative recrystallization foliation. The preferred orientation of tiny epidote inclusions in quartz (Fig. 5) are presumed to be the relics of primary deformative structure (s₁?). However, these phenomena can also be explained as the result of an alteration process that had taken place at an early stage of the mentioned process associated with s₂ planes.

Kyanite occupies 1 to 4 vol. % of the rock composition. It forms porphyroblastic grains, their average size being 1-2 mm in diameter and locally individual thin crystals up to 1 cm long may be observed. Twinned crystals occur scarcely, but irregular intergrowths of crystals can be observed more often. Kyanite is absent when quartz and muscovite are present in greater amounts. Occurrence of kyanite (Figs. 2-4) is limited to those samples, which contain much Mg-chlorite (over 85 %), thus indicating its formation in an environment of strong metasomatic reworking. The process of Mg-chloritization continued intensively, this being documented by the replacement of muscovite by chlorite (Fig. 3, lower margin) or the replacement of kyanite proper (Fig. 4 right).



Fig. 2. Kyanite porphyroblasts in Mg-chloritic matrix (magn. 30x, crossed nicols).



Fig. 3. BSE image of kyanite porphyroblast, pale flakes on the right — muscovite, dark-grey matrix — Mg-chlorite.



Fig. 4. Kyanite porphyroblast, replaced at the right side by Mgchlorite (BSE image).

Muscovite is straggled in amounts of 1-3 vol. % and occurs in the kyanite-bearing rock as relic blasts (Fig. 3 right next to kyanite) and also, partially as tiny recrystallized flakes and needles (Figs. 3, 4), which formed locally to copy the cleavage planes. In terms of metamorphic conditions, it is likely, that the newly formed muscovite crystallizes under retrograde conditions and its formation depends on certain addition (K_2O, Al_2O_3) as well as recrystallization within the frame of desintegration of the older muscovite generation (e.g. overgrowth of Mg-chlorite with muscovite to the left of kyanite in Fig. 4). A certain portion of the original muscovite should probably also be considered as forming due to older alterations, as it occurs in association with minute minerals of the epidote-zoisite group and quartz (it is a well known fact, that sericitization, silicification and saussuritization characterize the alterations of plagioclases in the granitoids and gneisses regionally). Tab. 1 displays orientation analyses of phengitic muscovites, whose tschermakitic substitution is marked by strong predominance of Mg over Fe (see relation M/MF, Tab. 1). Muscovite reflects its Mg saturation during allochemical alteration, but in a balanced stoichiometric relation. Increase of the octahedric Fe + Mg (FM) should be compensated by increased Si^{IV} as well as by the decrease of Al. This is in turn reflected by the decrease of the Na component in the A position of muscovite as commonly observed in natural specimens (e.g. Guidotti 1984). The chemical composition of presumed relics of older muscovite is analogous but displays at the same time similar variability, as is the case of newly formed minute

Table 1: Microprobe analyses of muscovite. Calculation based on 22 oxygens. FM = (Fe + Mg), and M/MF = Mg/(Mg + Fe) in structural formulae.

		MUSCOVITE		
	1	2	3	4
SiO ₂	48.24	47.72	47.54	47.83
TiO2	0.69	0.18	0.14	0.56
Al ₂ O ₃	34.17	37.84	35.63	36.05
FeOnt	0.35	0.09	0.25	1.22
MnO	0.01	0.04	0	0
MgO	1.37	0.41	0.53	1.47
CaO	0.05	0.07	0	0.07
Na ₂ O	0.7	2.23	1.36	0.36
K ₂ O	9.44	7.67	8.53	7.22
Total	95.02	96.24	93.98	94.78
SiIV	6.354	6.159	6.298	6.246
AIIV	1.646	1.841	1.702	1.754
AIVI	3.658	3.915	3.863	3.794
Ti	0.068	0.017	0.014	0.055
Feat	0.039	0.01	0.028	0.133
Mn	0.002	0.005		
Mg	0.27	0.079	0.105	0.286
Osite	4.037	4.026	4.009	4.268
Ca	0.008	0.01		0.01
Na	0.179	0.558	0.349	0.091
K	1.586	1.262	1.442	1.203
Asie	1.773	1.83	1.791	1.304
marg	0.451	0.55		0.767
par	10.096	30.5	19	4.860
ms	89.453	68.95	80.559	92.255
FM	0.309	0.158	0.133	0.411
M/FM	0.874	0.888	0.791	0.682

flakes, which indicates their common equilibration during the metasomatic process.

Quartz is present in variable amounts (ca. 3-7 %) and within a wide variety of textural types and crystallizes over a long period of time. Its undulatory extinction is generally low, hydrotermal activity probably healed up the older deformed crystals. The oldest generation formed prior to the Mg-metasomatism and this quartz obviously also represents a corrosive phase; it locally encloses planarily oriented phases (minerals of epidote-zoizite group, less Ti-Fe oxides), whose relics may still be seen in superimposed Mg-chlorite (Fig. 5). Quartz grains reach the size of up 1 mm, locally forming aggregates with a mosaic texture. During the hydrothermal after effects silicification took place, and penetrated into the chlorite matrix, replacing the kyanite etc.

Mg-chlorite—a predominant mineral, that forms at the expense of aluminosilicate rocks in a process of Mg-metasomatism. It developed within the whole range of allochemical metamorphic events, starting with crystallization along the s_2 foliation and ending by fine-grained Mg-chlorite, associated with quartz and sericite. The average size of flakes is 0.2 mm, however, they may reach locally the size of 1 mm. Larger



Fig. 5. Replacement of quartz by Mg-chlorite demonstrates influx of Mg and Al. Pale minute inclusions (oriented in ENE-WSW direction) are older deformation relics (BSE image).



Fig. 6. BSE image of grey Mg-chlorite replaces its lighter precursor (for caption see text and Fig. 7).

blasts probably formed after a certain pressure release has taken place, as they are often randomly oriented or crystallized passively within the pressure shadows of kyanite. Their crystallization in the environment of smaller, but chemically identical Mg-chlorites resembles the mechanism of the so called Ostwald ripening. Smaller post-kinematic rosette-like aggregates of Mg-chlorite also formed, or Mg-chlorite replaced the earlier crystallized kyanite (Fig. 4 right). The chlorites under study do not show any pleochroism and their interference colours are mostly pale-grey. Fig. 5 depicts a Mg-chlorite replacing an older quartz with inclusions. This structural phenomenon indicates at the same time considerable enrichment of Al, besides Mg. The scanning image (Fig. 6) displays the relics of brighter phases of Mg-chlorite (Tab. 2, analyses marked A), being replaced by dark-grey chloritic matter (marked B). Microprobe analyses have shown, that the differences in chemical composition of the two phases are negligible and expected increasing activity of Mg could not be demonstrated unambiguously. The most suitable indicator of chemical changes is the decrease of Al_{total} and slight increase in ratio Mg/(Mg + Fe) in younger dominant chlorite phases (Fig. 7). We consider it probable, that the released Al is not released from the system (see high content of Al₂O₃, Tab. 2 and 4), but may, apart from the reaction 2, also contribute to the formation of kyanite, or newly formed muscovite. According to Hey's classification, the chlorite is projected into the field of Al-rich sheridanite and in the case of chlorite 2 (Tab. 2) even to the boundary with korundophyllite.

Tourmaline — is always present, although its quantity varies (0.X-2 % of the volume of rock). It is present as tiny grains some 0.1 mm in size, disseminated in the chloritic matrix. The sections perpendicular to the c axis are almost colourless or have low interfraction colour tints of grey to beige. No growth zonality could be observed on the scan photographs. However, the variation in chemical composition at the margins vs. the centres of crystals (Tab. 3) follows the same trend as is the case in preceding chlorites. Although the analyses could have been to a certain degree mistaken and show slightly exaggerated values of SiO₂ it seems, that an increase in the content of Mg in respect to the contents of Fe and Al (Fig. 8), have taken place towards the centre of the grain. The decrease can also be observed in the sum of alkalis which, combined with distinct undersaturation of the X-position, agrees with the character of the metasomatic process. Tourma-



Fig. 7. Increase of Mg/(Mg + Fe) ratio and decrease of total alumina contents indicate trend of chemical evolution in the Mg-chlorites as shown in Fig. 6 and Tab. 2 (A — lighter-, B — darker phases).

Table 2: Composition of Mg-chlorites (formula calculation based on 28 oxygens) indicates small difference between older relics (A) and younger replacing phase (B), (see also Fig. 6).

Table 3: Composition of tournaline (based on 24.5 oxygens) evidences predominance of the dravite component (see Figs. 8 and 9).

CHLORITE						
	1A	1B	2A	2B	3A	3B
SiO ₂	28.94	28.54	26.37	27.28	28.28	28.16
TiO ₂	0.04	0.00	0.03	0.00	0.02	0.03
Al ₂ O ₃	26.83	25.11	26.09	25.50	24.52	24.41
FeOnt	5.24	5.36	5.97	5.47	6.11	5.81
MnO	0.00	0.12	0.22	0.10	0.00	0.37
MgO	26.40	28.39	30.18	30.95	28.74	28.51
CaO	0.01	0.03	0.01	0.08	0.01	0.06
Na ₂ O	0.00	0.00	0.00	0.03	0.00	0.00
K ₂ O	0.00	0.01	0.01	0.01	0.00	0.01
Cr ₂ O ₃	0.01	0.09	0.00	0.06	0.00	0.34
Total	87.47	87.65	88.88	89.48	87.68	87.69
SiIV	5.434	5.380	4.952	5.071	5.354	5.340
AJIV	2.566	2.620	3.048	2.929	2.646	2.660
AJVI	3.371	2.959	2.727	2.658	2.825	2.785
Ti	0.006		0.004		0.003	0.004
Feat	0.823	0.845	0.938	0.850	0.967	0.921
Mn		0.019	0.035	0.016		0.059
Mg	7.389	7.979	8.449	8.577	8.111	8.059
Cr	0.001	0.013		0.009		0.050
Osite	11.590	11.815	12.153	12.110	11.906	11.878
Ca		0.006	0.002	0.016	0.002	0.011
Na				0.011		0.001
к		0.002	0.002	0.002		0.002
M/MF	0.900	0.904	0.900	0.910	0.893	0.898
ME	8.212	8.824	9.387	9.427	9.078	8,980

		TOURMALINE	,	
	core	rim	core	rim
SiO ₂	37.8	37.67	37.38	37.88
TiO ₂	0.07	0.25	0.04	0.16
Al ₂ O ₃	34.67	33.75	34.76	34.74
FeOkt	1.39	1.08	2.13	1.12
MnO	0.03	0.14	0.02	0
MgO	8.5	9.5	8.24	8.51
CaO	0.13	0.29	0.14	0.12
Na ₂ O	2.01	1.86	1.082	1.76
K ₂ O	0	0	0	0
Cr ₂ O ₃	0.3	0	0	0.17
Total	84.89	84.536	84.525	84.45
SiVI	6.041	6.045	6.015	6.063
ALT	0.000	0.000	0.000	0.000
AIZ	6.000	6.000	6.000	6.000
Al Y	0.531	0.383	0.582	0.554
Ti	0.008	0.030	0.004	0.019
Fekx	0.186	0.144	0.287	0.150
Mn	0.004	0.019	0.003	
Mg	2.025	2.273	1.977	2.029
Cr	0.038			0.022
Y_{site}	2.792	2.849	2.853	2.774
Ca	0.022	0.050	0.024	0.021
Na	0.621	0.579	0.568	0.546
X _{site}	0.643	0.584	0.592	0.567
M/MF	0.916	0.940	0.873	0.931
MF	2.211	2.417	2.264	2.179

line has been classified as the dravite, what reflects the geochemical environment of its development. In the classifying — genetic scheme of Henry & Guidotti (1985) it is placed within the field of metamorphites coexisting with the aluminarich phase (Fig. 9, field 4). (The stippled field 7 documents a low content of Ca, however the proposed petrogenetic origin cannot be accepted in this case.) The effects of Mg metasomatism are also manifested by findings of scarce tourmalines containing 60 % of the uvite component (Bouška et al. 1973) within silicified zones at the nearby magnesite-talc deposit (some 1.5 km S from Hnúšťa).

Accessory minerals — apatite, monazite, zircon, various Ti-mixtures and relics of epidote (pale prolonged grains in Fig. 5) were identified using the EDAX. The formation of monazite (with semiquantitative composition: P_2O_5 18 %, ThO₂ 10 %, CaO 4 %, La₂O₃ 23 %, Ce₂O₃ 44 wt. %) is also related to metasomatic regime. Monazite and apatite are concentrators of LREE (Burt 1989), which explains their contents in the rock sample. Frequent occurrences of tiny grains of apatite are clearly assigned to the newly formed assemblage. However, some inherited grains of the stated accessory minerals cannot be ruled out, because of their common presence predominantly within the granitoids.

Bulk rock chemistry and element mobility

The whole-rock chemical analysis shows a unique geochemical composition of the rock under study (Tab. 4, first column) and is in good agreement with the petrographic data given in the previous chapter. To compare these data we present some representative lithotypes from nearby outcrops, which may constitute the precursor. Sample No. 2 is partly silicified and biotitized leucocratic aplitic muscovitic granite with garnet. In the third column there is an analysis of an altered granitoidic rock (micas are replaced by chlorite, feldspars are mostly preserved), whose initial composition probably resembled that in the analysis No. 2. The alterations are characterized by occurrence of pennine, clinozoisite and sericite, gradually replaced by faintly pleochroic Mg-chlorite. Granites, already displaying a variable constitution in their primary state, intruded the hornfelsic, garnetiferous biotite gneisses (No. 4), which are sometimes referred to as migmatites. Analysis No. 5-paragneiss (albitized garnetiferous muscovite biotite gneiss) collected north from the dislocation zone (Fig. 1B). The sixth column there are values of rockforming and trace elements in the "average pelite" (Shaw 1954, 1956).

Evaluation of the silicate analyses of kyanite — Mg-chlorite schist (Tab. 4a) immediately reveals that a significant decrease occurred in the contents of SiO_2 and the alkalies, notably Na. There is also a reduction in the content of Ca, Fe^{3+} , as well as Cl and F. Reduction of petrogenetic elements is usually accompanied by the decrease of Ba and, to a certain degree of Sr and Rb (Tab. 4b,c). These changes mostly demonstrate the absence of feldspars and biotite (indicated mainly by decrease of Rb). Quartz and white mica are present only in subordinate amounts and influence substantially the indicated depletion.



Fig. 8. Diagram showing relation between the Mg/(Mg + Fe) ratio and Al contents in structural position Y in tournaline (c — centre, r — rim) displays similar trend as in case of chlorite.



Fig. 9. Classification diagram of tourmaline (Henry & Guidotti 1985), field (4) metapelites and metapsammites coexisting with Al phase,(5) the same non coexisting with Al phase, (7) metaultramafics and Cr, V rich metasediments with low content of Ca. Hatched area within the field (7) represents analyses given in Tab.3.

Low contents of Cu, Zn, Ni and Co reflect primarily the absence of sulfides and, to a lesser extent, of micas. Sample No. 5 contains the same total amount of SO_3 but at the same time a higher content of these metallic elements is a good indicator of the former presence of micas (Ni, Co in biotite and Zn, Cu obviously in muscovite, too). The above features are mostly due to the diadochic properties of these trace elements.

A conspicuous increase in contents of Al_2O_3 , MgO, H_2O and also P_2O_5 and FeO can be observed in the rock-forming oxides. The increase of these components reflects significant chloritization due to the Mg-metasomatic process. Low contents of Fe₂O₃ indicate, that the Fe³⁺ is almost absent in the structure of chlorite. The phosphorus is bound to accessory apatite and monazite. The increase in Li content probably depends on the abundance of tourmaline and Ga increases due to abundance of Al_2O_3 .

Petrography and the above indicated geochemical behaviour of elements has been examined using the so called isocone diagram (sensu Grant 1986, Fig. 10). The isocones are radial lines connecting points of identical chemical concentration. The kyanite leucophyllite (CA) is plotted along the vertical axis, and the composition of leucocratic granite, as probable precursor of the rock under study, along the horizontal axis (C⁰, 2nd. an. in Tab. 4). The unit isocone, which marks roughly a constant volume (in agreement with specific densities 2.70 and 2.76 g/cm³ the slope of isocone should be 0.98) should indicate a mobility of practically all significant elements, Zr being the only possible exception. The model situation, which assumes that H2O and MgO are the most important constituents supplied in the system, infiltrate the rock at the expense of growing volume (isocone with the slope 0.78), cannot be accepted.

The majority of papers refer to Al₂O₃ as an immobile component during metamorphic or hydrothermal processes (Gresens 1967; Carmichael 1969; Kerrich et al. 1980; Grant 1986 — first three examples). The isocone 2.1 placed across Al₂O₃ also intersects, or passes nearby P₂O₅, FeO_{tot} and La with Ce. Assuming, that the above components are immobile, this should result in a volume reduction of about 50 %, which should correspond to removal of SiO₂, alkalies, CaO etc. (Fig. 10). However, great dispersion of depleted elements plotted below isocones and others, clearly supply elements above isocones do not allow us to accept the concept of an extensive volume reduction. Replacement of quartz (Fig. 5) or albiterich plagioclase by Mg-chlorite in the granite (an.3. Tab. 4.) indicates only a limited volume reduction (some 3 %, inferred from specific gravity after values of Hey 1954 and Robie at al. 1968). In general, on the basis of composition-volume analysis we presume that the information on metasomatic history of a rock could be placed between the isocones 1 and 2.1 (probably valid more for the trace elements bound on accessories), whereas the substantial volume balance took place close to the unit isocone.

There seem to be no clear regularities in the behaviour of the REE in metamorphic processes (Grauch 1989) and the case is even worse in metasomatic processes. Comparison with the reference samples (Tab. 4c, Figs. 10, 11) has shown, that the contrasting mobility of REE takes place during the metasomatic processes, which is effected by an addition of LREE and removal of HREE. The association of La, Ce and Sm with PO_4^{3-} anion in apatite and monazite is substantiated. Accumulation of LREE together with other components placed along the 2.1 isocone (Fig. 10) indicates a common geochemical process with supply of elements, however a certain role could also have been played by lower solubility of LREE relative to HREE in mineralized fluids (Mariano 1989). This postulate and the presence of garnet as the main HREEbearing mineral in all reference samples indicate that alterations have taken place along with synchronuous depletion of other incompatible elements (e.g. CaO, MnO).

The presented geochemical features are roughly correlable to alteration in host rocks of talc deposits in the French Pyrenees or in the Eastern Alps (Moine at al. 1982; Prochaska 1986). The rock under study represents the end product of Mg-metasomatism — practically all elements were mobile. On the basis of field relations, petrographic features (e.g. relic muscovite blasts) and good correlation with comparable occurrences in the Alps we propose the muscovitic granite as being the most probable protolith of the rocks under study. It can



Fig. 10. Relationship between chemical composition of kyanite-Mgchlorite schist (\mathbb{C}^A) and leucocrate muscovite granite - \mathbb{C}^0 (sample 2 in Tab. 4) in the isocon diagram (according to Grant 1986). Contents of some components is due to clear illustration multiplied or divided by integers. Contration of trace elements are given in ppm (circles).



Fig. 11. Normalized curves of REE (see Table 4c) indicate an increase of LREE and decrease of HREE in studied sample. *Symbols*: circle — kyanite-Mg-chlorite schist (sample 1 in Fig. 4c); cross — muscovite granite (sample 2); asterisk — altered granite (sample 3); triangle — hornfelsic gneiss (sample 4); square — paragneiss (sample 5).

be presumed that the components removed from the rocks during Mg-metasomatism have only migrated over relatively

Table 4: a —, **b** — Whole rock analyses of rock-forming and trace elements. Sample 1 — ky- Mg-chloritic schist; Sample 2 — leucocratic muscovitic granite; Sample 3 — hydrotermally affected granitoide rock; Sample 4 — hornfelsic garnetiferous-biotitic gneiss; Sample 5 — albitized garnetiferous-biotitic gneiss; Sample 6 — "average metapelite" (Shaw 1954, 1956). **c** – REE an. CH — average chondrite (Boynton 1984) used to normalize other analyses (see Fig. 11).

a)	1	2	3	4	5	6
SiO ₂	35.39	76.04	58.75	69.8	70.66	61.54
Al ₂ O ₃	24.41	11.64	18.1	13.66	13.01	16.95
FeO	4.72	1.72	4.67	3.06	3.1	3.9
Fe ₂ O ₃	0.38	1.02	2.29	1.04	1.2	2.56
CaO	0.49	1.11	0.92	0.39	2.24	1.76
MgO	24.34	1.1	4.34	2.47	2.41	2.52
TiO ₂	0.56	0.47	1.04	0.66	0.65	0.82
P ₂ O ₅	0.27	0.11	0.35	0.15	0.19	
MnO	0.025	0.045	0.044	0.025	0.079	
Na ₂ O	0.26	2.29	4.04	3.8	2.88	1.84
K ₂ O	0.73	1.64	1.28	0.92	2.12	3.45
SO ₃ T	0.02	0.1	0.04	0.05	0.02	
F	0.004	0.05	0.07	0.01	0.007	
a	0.002	0.01	0.01	0.01	0.007	
CO2	1.34	1.21	1.33	1.11	0.5	1.67
H ₂ O ⁻	0.55	0.04	0.15	0.23	0.54	
H_2O^+	4.96	0.75	2.11	2.59	0.08	3.47
Total	98.45	99.7 7	99.59	99.96	99.7	100.48
						An real for a local de la companya d
b)	1	2	3	4	5	6
Sr	80	180	80	40	280	710
Ba	11	570	296	308	518	
Li	14	4	12	10	18	55
Zz	185	181	180	197	188	200
Nb	3	5	9	7	3	
Ga	40	1	30	1	30	19

<u> </u>	100	101	180	197	100	200
Nb	3	5	9	7	3	
Ga	40	1	30	1	30	19
Cu	1	4	1	7	7	18
Zn	1	30	40	39	60	
Ni	3	8	4	24	22	64
Co	3	8	12	4	6	18
v	70	62	130	90	65	120
Мо	5	6	10	5	1	
W	15	6	15	5	10	

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c)	1	2	3	4	5	CH
La	57.3	30.5	32.1	46.7	31.9	0.31
Ce	105	50.7	53.9	74,5	75.6	0.81
Sm	7.28	4.69	6.29	7.52	4.66	0.195
Eu	0.72	1.12	1.06	1.42	1.19	0.074
Тъ	0	0	0	0.8		0.047
Yb	1.21	1.8	3.4	3.1	3.04	0.2
Lu	<0.2	0.3	0.3	0.52	0.42	0.3
Rb	28.7	71	37	107	121	

short distances, because the other deformed rocks in the central part of the Sinec Massif are affected by distinct secondary albitization, muscovitization and partly by development of biotite and clinozoisite.

Estimation of metamorphic and mass transfer conditions

In an Al saturated system characterized by depletion of silicon and alkalies, there developed favourable conditions for kyanite to form. The texture (see Fig. 3) and the type of metasomatism indicate, that a reaction similar to that, observed in the Eastern Alpine leucophyllites (Friedrich 1947; Vendel 1972), should be expected:

$$2 K_{2}Al_{4}(Si_{6}Al_{2}O_{20})(OH)_{4} + 5 MgO = (ms)$$

= Mg_{5}Al_{2}(Si_{3}O_{10})(OH)_{8} + 5 Al_{2}SiO_{5} + 4 SiO_{2} + 2 K_{2}O (2)

(Mg-chl)

(*ky*)

 (\bar{Q})

This reaction should however imply, that concurrently forming quartz would have to be removed from the rock under study. The formation of kyanite requires not only a favourable fluid flow, but also maintainance of the uppermost metamorphic conditions as is also indicated by the evolution of the Aldistribution of chlorite (Fig. 7). Considering the univariant curve of stability of the kyanite/andalusite sensu Holdaway (1971), kyanite forms from pyrophyllite under conditions of $a_{H,O} = 1$ at 380 °C and 2 kb, but the reaction, which involves diaspore already runs at 360 °C (Fig. 12, Haas & Holdaway 1973). It may be possible to relate the high concentration of aluminium in the studied sample to the Al-saturated environment with diaspore. Considering that circulation of metasomatic fluids takes place, the questionable nucleation temperature, which requires under standard conditions the so called thermal overstepping above the lower boundary of mineral stability, should not pose any serious obstacle in estimating the temperature conditions. Another problem is posed by the possible presence of CO2 in the fluid, which should lower the temperature at $a_{H_2O} = 0.\overline{8}$ by about 20 °C (Thompson 1971). Thus the temperature assumed for kyanite formation may be estimated at 350-400 °C, which agrees with the chlorite geothermometer, derived from recent geothermal systems (Cathelineau 1988). The calculated temperature range from 355 to 420 °C is based on Al^{IV} content in the structural formula of chlorite (Tab. 2). The correction applied in the thermometer to counteract the Al oversaturated environment (Kranidiotis & MacLean 1987) would result in an increase of the temperature by 20 °C.

The pressure conditions in hydrothermal systems are generally variable and furthermore, in evaluating the pressure of the low metamorphism, the external fluid pressure (Holdaway & Goodge 1990) plays an important role in relation to the thickess of the lithological overburden. As no transformation of chlorite into talc (sensu Massonne & Schreyer 1989) was found either in the studied assemblage or in any other aluminosilicate rock, a high-pressure genesis is not assumed. The contents of celadonite component in the muscovite (FM, Tab. 1) were computed into the bo parameter, using the regression equation of Guidotti et al. (1989). Applying the semiquantitative baric classification of Guidotti & Sassi (1986) and maintaining the above temperatures, the values correspond to 2.3-4 kb. All the statements above indicate, that we are dealing with lower- to middle pressure conditions which, apart from presumed outer fluid pressure, resemble those of the barrowian metamorphic type.

The above mentioned P-T estimates agree with the character of alterations of the surrounding country-rock, however such a coincidence in fluid composition etc. are missing, which would lead to formation of such an unusual assemblage. It cannot be excluded, that similar conditions prevailed during the steatitization reactions, which we envisage to be synchronous with the origin of the assemblage studied. To keep reaction (1) running, the CO₂ must be taken away from the system, which is facilitated by tectonic disruption of mag-



Fig. 12. p-T-X diagram with reactions (Hass & Holdaway 1973): 1 — pyrophyllite + diaspore = 4 kyanite + H_2O ; 2 — pyrophyllite = kyanite + 3 quartz + H_2O . Stippled orientatively deliminates the area of p-T estimations based on chemical composition of Mg-chlorite and muscovite, arrows in lower part of the diagram illustrate influx and removal of elements during the metasomatic process.

nesite bodies. The overwhelming influx of the Mg into the rock under study was very probably due to a surplus of Mg, released during the magnesite steatitization. The talc scales copy the rhombohedral texture of magnesite (Kužvart 1955), indicating, that the reaction was isovolumetric and this implied the escape of excessive Mg. Magnesite decomposition, operated by permeation of fluids through the zones, in which, due to kinetic, chemical, time-bound or other reasons, no talc formation has taken place (forming only quartz, calcite etc.) should be regarded as the main Mg source. In this case, as in other areas kyanite associates with Al-sheridanite and not with sheridanite-clinochlore (Moine et al. 1989), which suggests, that there exists a strong dependence of the Al mobility upon the Mg presence in the fluid phase. According to the activity diagrams of Helgeson (1978), the evolution in the succession feldspar-muscovite-Al-silicate in a system Na2O-K₂O-Al₂O₃-SiO₂-H₂O operates under conditions of an acid environment, favoured by removal of Si from the rock (Hemley et al. 1980). As the data regarding the dependence of Al mobility on the pH level in a hydrothermal process are incomplete and often ambiguous, we tend to accept the more conventional case with the lower pH. Supply of LREE give evidence rather in favour of the activity of acid chloride fluids, whereas the HREE are predominatly mobilized in CO_3^{2-} and F⁻ fluids (e.g. McLenan & Taylor 1979; Vocke at al. 1987). Lack of Fe³⁺ in the rock studied probably indicates reduced oxygen potential during the metasomatism. Fig. 12 displays approximate P-T conditions, along with a generalized outline of the supply and removal of the elements.

Regional implications

The only pre-Alpine kyanite indication presumed to occur within the area of the southern Veporic Unit (the so-called Kohút Zone) crystalline rocks are sericitic pseudomorphs in metapelites primary enriched in aluminium and iron (Kováčik 1991). Méres & Hovorka (1991) assign the formation of minute kyanite with staurolite in the micaschist-gneiss complex, which crops out north of the above mentioned occurrence, to the Alpine orogeny. In agreement with the Alpine structural scenario of the lower degree metamorphites and the Alpine age of talc deposits (Abonyi & Abonyiová 1981), it is also accepted the Alpine age of the mineral assemblage under study. The geological implications indicate, that the age of magnesite formation predates both the talc formation and the Cretaceous metamorphism.

The kyanite-Mg-chlorite-dravite metasomatic assemblage should form under slightly higher conditions, compared to the regional metarnorphism of the Mesozoic cover of southern Veporic Unit, limited to lower zones of the greenschist facies (Vrána 1966), or 300-350 °C (Plašienka et al. 1989). Local higher hydrothermal-metamorphic activity will therefore be accompanied to certain degree by thermal elevation resulting in increased heat flow.

Within the Gemeric Carboniferous sequence, which fringes the Veporic Unit from the SE (Fig. 1B), randomly oriented porphyroblasts of chloritoid were observed as well as more scarcely kyanite. The occurrence of kyanite is usually bound to the presence of Mg-chlorite and does not appear in association with feldspars (Vrána 1964). This petrographic information seems to be an analogy to our case and, at the same time, it could explain the question, why the sericite-quartzose schists of the Mesozoic cover are free of kyanite and/or chloritoid. The Carboniferous Gemeric sequences, which crop out in a tectonic superposition over the Mesozoic Veporic cover, include magnesite bodies (in the northern parts there is siderite in turn) and large masses of black shales with organic matter, which may have released, during the Alpine tectonometamorphic events, the CO2, CH4, MgO and so forth which infiltrated the neighbouring beds. Several observations refer to the strong influence of CO₂-fluids and the dominant position of Mg in the formation of kyanite (e.g. Vrána 1975; Schreyer 1977) as well as the above mentioned reaction (2). Both, the presence of magnesite-talc lenses (in the case of Sinec Massif between two units of crystalline rocks) and the geological position of the rock studied indicate certain features in common with the Carboniferous Gemeric Complex.

Steatitization of magnesite along with the characteristic metamorphism of the Permian-Mesozoic cover of the Veporic Kohút Zone indicates an important influence of tectono-thermal reactivation of the Veporic basement. This is not only manifested by postkinematic blastesis of phyllosilicates, but also by rare green amphibole (tschermakite), which was recently dated on the host rock at 87.4 ± 2.6 Ma (plateau age), using Ar^{40}/Ar^{39} method (Kováčik & Maluski 1994). Rejuvenization of the basement deep within the crust, often associated with allochemical reactions may affect the character of the Alpine metamorphism, to a significant degree, without an assumption about lithostatic pressure of hypothetical tectonic overburden.

Conclusions

The newly formed kyanite developed in assemblage with Mg-chlorite (75-90 vol. %) and dravite due to Mg-metasoma-

tism of an aluminosilicate precursor rock (probably granite) of the Southern Veporic basement. Kyanite, which occurs very scarcely within the crystalline of the Kohút Zone, is bound to the Al-Mg saturated environment and the mechanism of its formation approaches that in the reaction (2). The development of the chemical composition of chlorite (Al-sheridanite) and dravite, shows a tendency to increase the ratio Mg/(Mg + Fe) and to decrease the content of Al during the late phase of metamorphism. The P-T conditions range between 350-420 °C and 2.3 to 4 kb, however, the uppermost metamorphic conditions were largely influenced by both, the favourable fluid flow and the tectonic predisposition of the surroundings of the talc-magnesite bodies. The mineral and the whole rock composition point out supply in contents of Mg, Al, H₂O, FeO_{tot}, P₂O₅, Li, Ga, LREE and removal of Si, Na, K, Ca, Rb, Ba and HREE, too. The metasomatic process (bound to the steatitization and hydrolysis of magnesite) probably occurred under lower pH and reducing conditions. These processes, associated with the fluid infiltration indicate some features in common with formation of kyanite and Mg-chlorite in the Gemeric Carboniferous. Tectono-thermal and mass transfer reactivation of the Veporic basement had played an important role in the Alpine metamorphism.

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