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IS VOLCANIC MATERIAL PRESENT IN THE MIDDLE TRIASSIC BASIN SEDIMENTS OF THE HRONIC UNIT (CHOČ NAPPE, WESTERN CARPATHIANS)?

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Abstract: The article is concerned with the problem of the occurrence and influence of Middle Triassic volcanic activity in the Reifling intra-platform depression pelagic sediments of the Choč Nappe (Hronic Unit), Central Western Carpathians. The results of the clay and accessory minerals, chemical and mineral composition of clay layers from five selected sedimentological profiles are combined in this work. In comparison with data from neighbouring regions - the Northern Calcareous Alps, Southern Alps, Hungarian Block and Dinarides, where the Middle Triassic volcanic rock products are known and documented, the area of the Central Western Carpathians was distant from the centres of this volcanism. This was probably the main reason why the presence of Middle Triassic volcanic products in the Choč Nappe sediments has not been unambiguously proved. We suggest, that in area of the Hronic Unit, the distant volcanism of neighbouring tectonic zones has been manifested only indirectly in the lithological and facial composition of the pelagic carbonates and the mineralogical and chemical composition of the clay fraction.

Key words: Western Carpathians, Middle Triassic, Hronic Unit, clay minerals, basin facies, chemical composition.

Introduction

During study of the Triassic pelagic sediments of the "Reifling Depression" (Masaryk 1990; Masaryk et al. 1993; Michalík et al. 1992; Lintnerová 1993; Lintnerová & Hladíková 1992) we encountered the view that the grey-green clayey-carbonate layers in the Reifling Formation, are, or could be of volcanic origin. This view is mostly supported by the published results of study of the Reifling Formation in the Northern Calcareous Alps (Bechstädt et al. 1976; Plöchinger & Wesender 1965), work from Hungary (Cros & Szabó 1984; Balogh 1981; Calegari & Monese 1964; Carraro & Fiora 1974; Cros 1980, 1982).

Sporadic data about the presence of volcanic-tufitic material in the Silica Nappe of the Western Carpathians also supports this view to a less degree (Mello 1974; Bystrický et al. 1988). Havrila et al. (1988) mention the presence of volcanic material in the Choč Unit (Turík profile), and occurrences of volcanites and pyroclastics are known in the surroundings of Poniky near Banská Bystrica, in the Choč Nappe and the Drienok Nappe (Hovorka & Spišiak 1988).

The aim of this work is to more exactly work out the composition and assess the origin of the "green" clayey-calcareous layers in the Reifling Limestone Formation of the Choč Nappe. The obtained mineralogical and petrographic data are significant from the point of view of assessing the extent of Middle Triassic volcanism. It is also possible to use the data in paleogeographical interpretation of the arrangement of the Triassic sedimentary area.

Geology

The Choč Nappe (Hronic Unit) covers a relatively extensive area in the Choč Mts., Nízke Tatry Mts. and Strážov Mts.. It is also present to a smaller extent in other ranges of the Central Western Carpathians. The sedimentary part mostly consists of Triassic carbonate formations, with a total thickness of 1500 to 2000 m.

This thick Triassic complex, mostly carbonate formations, is litho-facially close to the sequences of the nappes of the "Tirolicum" of the Northern Calcareous Alps. The carbonate sequence frequently overlies the partial Šturec Nappe (second tectonic unit of the Hronic Unit), the base of which includes a thick volcano- sedimentary complex of the Upper Carboniferous to Lower Triassic Ipoltice Group ("Melaphyr serie") together with a mostly shallow-water dolomite rock development of the Middle to Late Triassic age.

The siliciclastic Benkov and Šuňava Formation of Early Triassic age forms the base of the Choč Nappe. A thick Middle to Upper Triassic carbonate sequence forms the main lithological content. Both shallow-water formations of a carbonate platform (Lower to Middle Anisian, or Upper Carnian-Rhaetian), and sediments of deep intraplatformal depressions (Upper Anisian to Julian) are present here. The presence of basin and slope hemipelagic to pelagic sediments of the Reifling, Svarín and Lunz Formations, among shallow water shelf limestones and dolomites (Annaberg, Gutenstein, Raumzau, Oponic, Hauptdolomite, Dachstein and Hybe) is a characteristic phenomenon, distinguishing the complex from other Triassic sequences in the Western Carpathians.

Middle Triassic volcanites

Tufites and volcanites in the Middle Triassic sediments of the Central Western Carpathians

Probable primary or redeposited occurrences of volcanic material are unknown up to now in the Middle Triassic sediments of the Central Western Carpathians. Sporadic occurrences have been published only from the Reifling and Mürztal Formations of the Silica Nappe (Mello 1974; Bystrický et al. 1982), but its sporadic occurrence is not more closely placed.

In south east part of Banská Bystrica area, near the settlement of Poniky, Hovorka & Slavkay (1966), Slavkay (1979), Hovorka & Spišiak (1988), studied and described a small basic volcanic body of phlogopitic picrite rocks among Triassic dolomites assigned to the Choč Nappe. Phlogopitic picrite rock has no equivalent among the basic rocks of the Mesozoic of the Western Carpathians. In the above mentioned work, it is considered as an intrusion of picritic volcanites, after the movement of the Carpathian nappes (after the Lower Cretaceous), and doubt is cast on the assignment of the dolomites to the Choč Nappe.

South east of the Banská Bystrica area, the Drienok Nappe occurs, practically overlying the above mentioned sequence of dolomites and picrites (Bystrický 1966, 1972). According to Hovorka & Spišiak (1988), the volcanic rocks of the Drienok Nappe belong to three basic types, that is rhyolites, trachytes and andesites. The presence of various types of pyroclastics is characteristic of the whole volcanic complex. The presence of ignimbrites, which points to a dry land environment for the origin of the volcanites, or their extrusive equivalents, is interesting. Some volcanic formations of the Inner Western Carpathians from the Bükk Mts. are close to them in material, but different in age (uppermost Lower Triassic, against Middle to Upper Triassic).

Middle Triassic tufites in the sediments of the Northern Calcareous Alps

Occurrences of "green layers", representing redeposited fine microcrystallic material of pyroclastic character, found in the pelagic sediments of the Reifling Formation, are described here (Bechstädt et al. 1976; Köbel 1969; Plöchinger & Wesender 1965). On the basis of mineralogical composition (sanidine, biotite, acidic plagioclase) these are products of an acid to intermediate character (Cros & Szabó 1984). Proximal tufites (Köbel 1969) have been described from the Arlberg district. Otherwise only distal tufites, redeposited from distant sources are known from the whole area of the Northern Calcareous Alps. The source areas for the volcanic materials were in the southern zones outside the actual Reifling Basin. Numerous occurrences of volcanoclastics and individual volcanites are known from the areas of the Southern Alps, Dolomites, Central Danubian Range, Bükk Mts. and the Dinarides.

The Middle Triassic tufites and volcanites of the Southern Alps

In the area of the Southern Alps, numerous occurrences of both redeposited pyroclastics of the "pietra verde" type in the framework of the Livinallongo (Buchenstein) Formation, and also layers of ignimbrites and individual volcanic rocks, are known (Calegari & Monese 1964; Carrero & Fiora 1974; Cros 1980, 1982; Cros & Fryssalakis 1982; Cros & Houel 1983). The varied range of alkaline-calcareous volcanic rocks includes rhyolites, dacites, trachytes, andesites and basalts. The first tufite layers are of Late Anisian age, but the main phase of volcanism is Ladinian. The mainly southern directions of transport of volcano-clastic material into the pelagic basins indicate that the source of the volcanic activity was in the area between the Central and Southern Alps.

The Inner Western Carpathians – the Balaton region and Bükk Mts.

In the area of the Central Danubian Range and Bükk Mts., layers with volcanites and pyroclastics of practically the same age (Late Anisian to Early Carnian) are known. They are very similar in mineralogical character to the volcanites of the Southern Alps (Szentpetery 1937; Szabó & Ravasz 1970; Ravasz 1973; Cros & Szabó 1984). Three successive phases of volcanic activity were identified here: 1 - weak in the Illyrian, 2 - main in the Fassanian and 3 - an insignificant one during the Late Ladinian to Early Carnian. In the Bükk Mts., andesite-basalt volcanism prevails, with occasional acidic eruptives, with a character close to the production of classic stratovolcanos. In the Balaton region, proximal types of tufites of the Late Anisian age have been described. According to the work of Cros & Szabó (1984), they paleogeographically represent the transitional member between the northern and southern Alpine provinces.

Methods

The revision of the sedimentary filling of the Reifling Depression of the Hronic Unit of the Western Carpathians is the result of field and laboratory study in recent years (Masaryk et al. 1993), with the use of some older works, mainly stratigraphical ones.

The clayey layers in the Reifling Formation were studied, both petrographically and by special methods (clay minerals, accessory minerals, chemical composition). The beds belong to the member of the Reifling Formation, known as nodular cherty limestones (Knollenkalk). The samples come from the profiles Turík, Matiašovce, Svarín, Zámostie and Malá Čierna (Figs. 1, 2), which were mostly evaluated in the work of Masaryk et al. (1993). Therefore we will not devote attention to the questions of sedimentology and stratigraphy, but we will concentrate only on some basic data about the litho-facial character of the chosen samples, and their position in the framework of the Reifling Formation.

Fine-grained separated samples were used for mineralogical and chemical study. The rock samples were crushed and sieved for the fraction less than 0.2 mm, and the fraction less than 2 μm was separated by the sedimentation method from this fraction. Before separation, the samples were desintegrated by ultrasonic probe. The carbonate minerals (cements) were removed by using acetate buffer, and organic material by heating in hydrogen peroxide. In all cases, clay material was analysed in the homoionic Na-form. The excess ions were removed from the samples by dialysis, before X-ray diffraction analysis. The oriented preparations for X-ray diffraction were prepared by sedimentation on glass slides. They were analyzed in the air dry state, after saturation with ethyleneglycol - EG (6 hours in EG vapour at a temperature of 60 °C).

Unoriented powder samples were prepared from unseparated samples, and from the sample fraction less than 2 μm. The fine

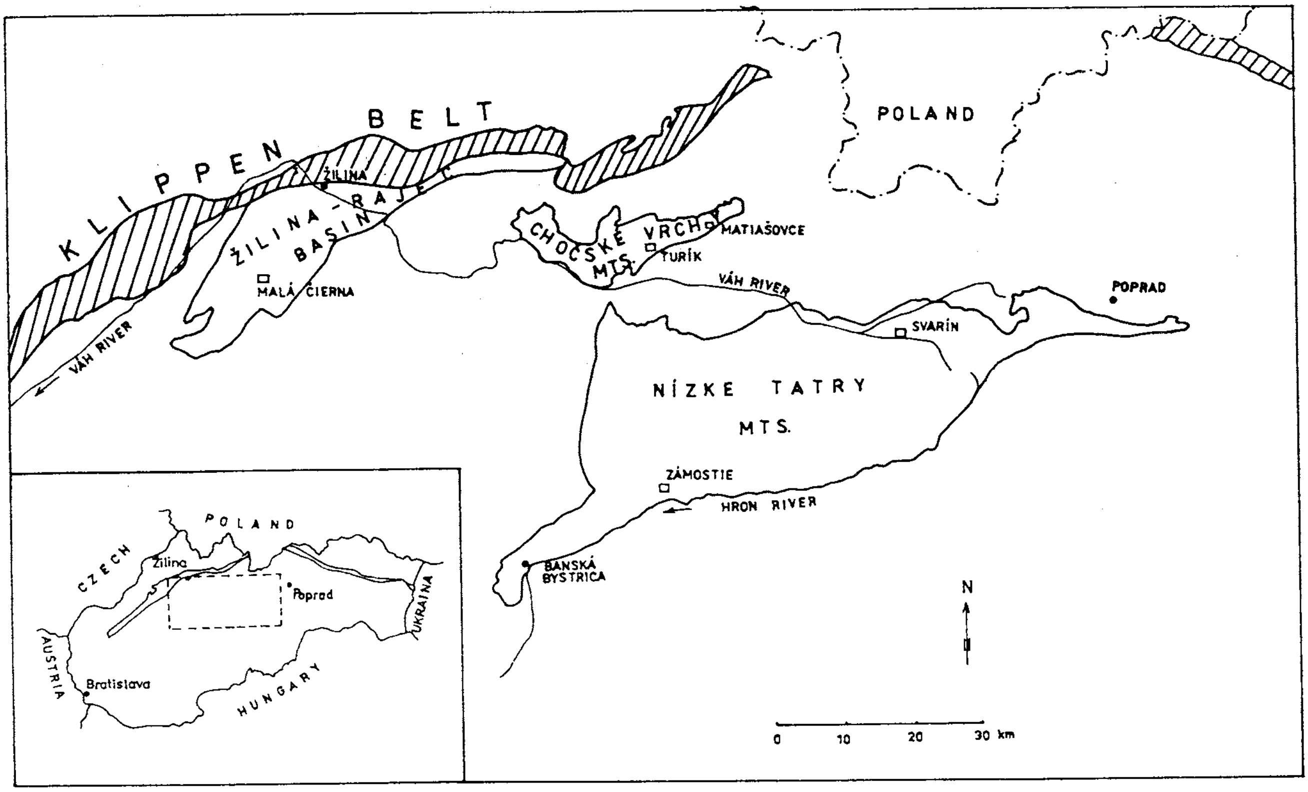

Fig. 1. Location map for the selection of samples and profiles.

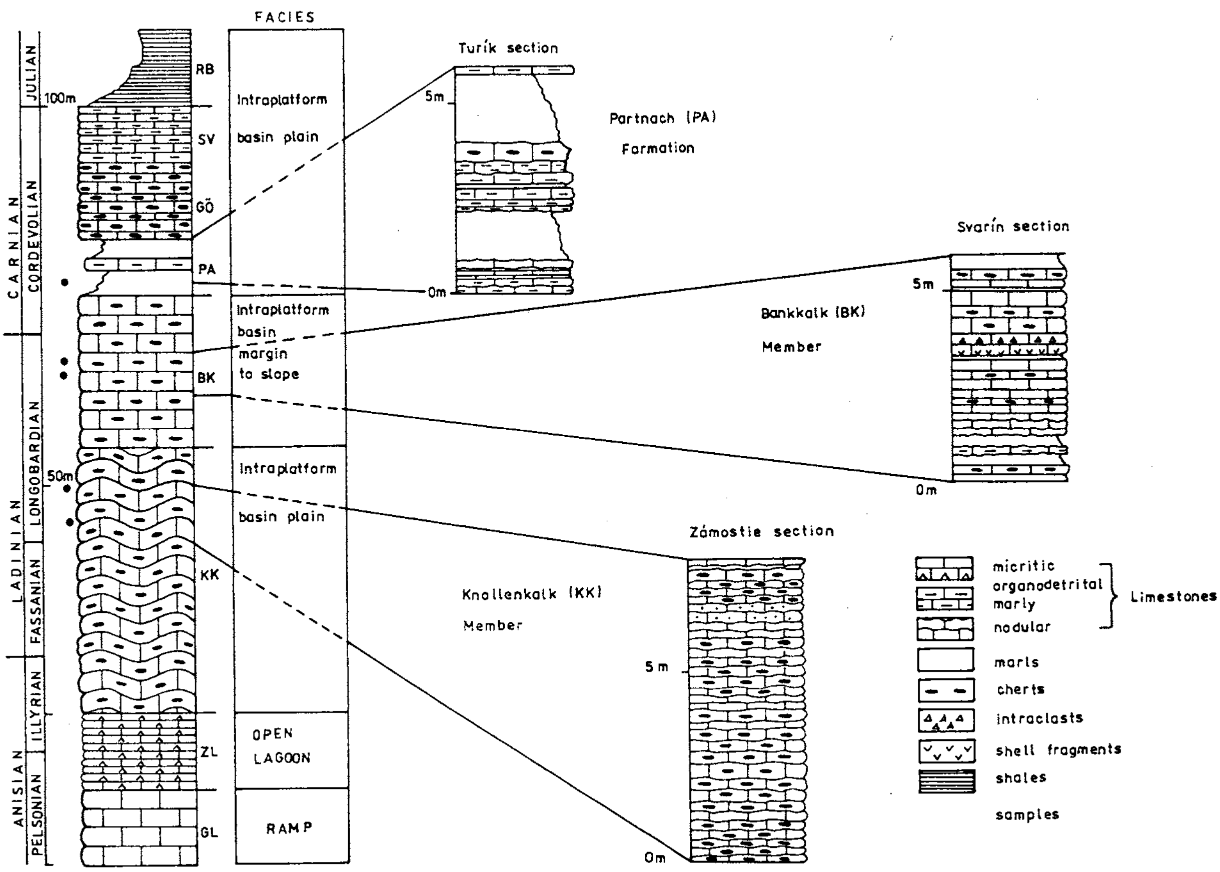

Fig. 2. Idealized profile of the formations of the Reifling Depression in the Hronic Unit.

fraction was mixed with a small quantity of quartz internal standard, and its record served on the determination b_o parametre. The X-ray diffraction analyses were performed on the X-ray diffractometer Philips PW 1050/25, using CuKα radiation (Ni filter).

From approximately 1 kg of rock sample, decanted samples were prepared for the identification of accessory minerals. Identification was done by optical methods.

The trace elements (in the clay fraction and in the rock samples) were analyzed by optical emission spectroscopy (OES), using the spectrograph PGS-2, in the ultraviolet and visible areas (Medveď et al. 1991). The results were checked by analysis of the standard reference sample KK (kaolinite, Karlovy Vary).

Results

Petrographic study

The limestones immediately underlying and overlying the marls are thin-bedded to slab-like (Fig. 2), and significantly nodular with numerous cherts of varying shape and size. Dark shades of grey and brown colour with intercalations of brown-green to ochre-green irregular laminae of calcareous marls prevail. The limestones are biomicritic (radiolarian-filament), weakly recrystallized, bioturbated and partly dolomitized.

The marls form several thin layers (max. up to 4 m), and frequently contain beds of varied marly limestones. The matrix is microcrystalline clayey carbonate with a significant content of secondary pyrite, and the products of its oxidation - limonite. In comparison with the surrounding limestones, the marls have a very low proportion of organic detritus. Relatively uniform dolomitization in the form of scattered idiomorphic rhombohedra of dolomite, reaching up to 30 % of the volume of the rock in some samples, is a characteristic feature.

Mineral composition

From X-ray diffraction analysis of oriented and unoriented powder preparations, we found that the studied rocks are composed of carbonates, quartz and clay minerals. Among the carbonate minerals, calcite and dolomite were identified from all the localities except Matiašovce. In samples from this locality, we identified only calcite by X-ray diffraction. All the samples had accessory contents of pyrite and marcasite. Apart from these two minerals, no other accessory minerals were identified in the heavy fractions.

The composition of the clays was studied in detail in the separated grain fraction less than 2 μm. The semi-quantitative composition of this fraction is given in Tab. 1. It is clear, that the dominant clay mineral in the studied samples is illite. In the sample from Zámostie, illite is the only mineral phase of the clay fraction. The presence of corrensite - a mixed-layer mineral of chlorite and smectite, at two localities - Matiašovce and Svarín, is interesting. Corrensite was identified in the samples by comparison of experimental basal reflexes (Fig. 3), with calculated reflexes (Reynolds 1988). The third clay mineral which occurs in the samples is kaolinite. The samples from the localities of Turík and Svarín have a moderately higher content of kaolinite (Tab. 1).

The illites from all the localities have relatively similar properties. The data given in Tab. 2 also documented this. The very low values of the Ir index (Srodon 1984), which represents the ratios of the intensities of the basal reflexes 001 and 003 in the air dry state, and after saturation with EG, indicate the absence of expanding layers. On the other hand, the relatively high values of the width in half-height of the first basal reflex of illite, which is known as the crystallinity of illite, points to a low grade postsedimentary alteration of the rock, and many structural stacking faults in the illite. The existence of stacking faults in the structure of the illite crystals also confirms the diffusional character of the 111 and 121 reflexes. The polytypes 1M and $2M_1$ were identified by an analysis of the non-basal illite reflexes. The values of the b_o parametres point to a relatively higher content of Fe in the structure of the illites (Smoliar & Drits 1988).

Trace elements

In the clay fraction less than 2 μm, the elements, of which the values are given in Tab. 3, were analysed by optical emission spectroscopy. The contents of Mo and Sc were below the threshold value of 3 ppm, and the content of La was under 30 ppm (the threshold of determinability for the instrument). These ele-

Table 1: The relative content of clay minerals in the studied samples determined by X-ray diffraction analysis. * - major phase, ○ - minor phase, ● - trace phase.

Sample	Illite	Kaolinite	Corrensite	Quartz
Matiašovce	*	●	○	
Turík	*	○		●
Svarín	*	○	○	●
Zámostie	*			
M. Čierna	*			●

Table 2: Comparison of the properties of illite from the studied samples. Ir - ratio of the intensities of the basal reflexes 001 and 003 in the natural and EG states, CI - crystallinity of illite, b_o - lattice parameter, N - not analyzed.

Sample	Ir	CI	b_o	Polytype modification
Matiašovce	1.12	0.60	9.016	$2M_1 > 1M$
Turík	1.00	0.45	9.030	$2M_1 > 1M$
Svarín	1.08	0.52	9.027	$2M_1 > 1M$
Zámostie	1.26	0.83	9.024	$2M_1 > 1M$
M. Čierna	1.16	0.72	N	N

Table 3: Content of traced elements in the clay fraction. Values expressed in ppm.

Sample	Ba	B	Mn	Pb	Ga	V	Cu	Ni	Zr	Y	Cr	Sr
Matiašovce	188	156	188	7	18	166	60	54	206	11.1	72	19
Turík	184	153	211	6	19	180	70	54	201	9.8	78	29
Svarín	176	139	188	12	17	121	78	46	179	10.8	73	19
Zámostie	173	154	262	22	20	128	112	73	301	20.4	54	18
M. Čierna	190	190	128	3.7	19	15	38	46	74	2.9	158	25

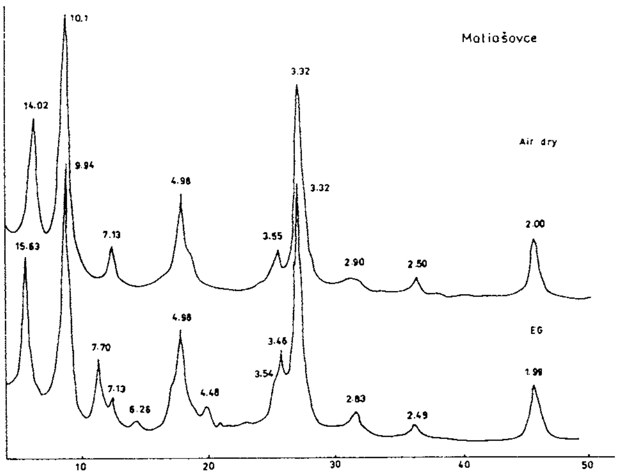

Fig. 3. X-ray diffraction record of the clay fraction of the sample from Matiašovce.

ments are not included in Tab. 3. In general, it is possible to say that the contents of the traced elements are more or less comparable from all the localities. Only the contents of vanadium and chromium from the locality of Malá Čierná are different. Great similarity in the contents of individual elements points to the source material and the sedimentary diagenetic conditions of the studied rocks being very similar (see Masaryk et al. 1993).

Discussion

Pelagic limestones with relatively equal conditions of sedimentation, especially a relatively low sedimentation rate, reliably reflect the important events caused by external influences. This could be precisely the addition of volcanic material, or the accompanying influences of volcanic activity on climate, biotopes and so on the development of organisms, which again have an influence on the lithofacial character of the sediments.

Petrographic study of the rocks does not offer direct evidence, which would unambiguously confirm the presence of volcanic material in the Reifling Formation, in contrast to the development of formations of the same age, in sedimentary zones further south (Fig. 4). The works which are concerned with the problem of Middle Triassic volcanism, in the area of the Eastern and Southern Alps, or the Inner Western Carpathians (Cros 1980, 1982; Cros & Houel 1983; Cros & Fryssalakis 1982; Cros & Szabó 1984; Szabó & Ravasz 1970) prove that significant volcanic activity had several independent phases with a maximum in the Lower Ladinian. The mineralogical-chemical composition of the volcanic products confirmed the alkaline-calcareous character, with a relatively varied series of volcanic and pyro-clastic rocks. The products of acidic intermediate and basic volcanism (rhyolites, trachytes, andesites, basalts) are also present here. The type of volcanism according to the cited works, is comparable to the island arcs with stratovolcanic centres. The centre of volcanic activity has been placed in the zones between the Central Alps or Carpathians, and the Southern Alps or Inner Carpathians on the basis of evaluation of proximality and current directions.

Occurrences of distal products, mostly tufites, from the Northern Calcareous Alps and the southern zone of the Central Carpathians, confirm this view. Classic criteria could not directly confirm the presence of volcanic (metamorphic) rocks, at any of the localities studied. However the petrographic studies do not completely exclude the presence of dispersed volcanic material - ash or redeposited volcanic material. Therefore we devoted increased attention to the mineralogical composition of the clay fraction of the clayey-calcareous layers. The works, which have devoted more detailed attention to mineralogical study of the changes of volcanic rocks and ashes from formations of various ages, show that the alteration of volcanic material creates a characteristic association of minerals. The presence of pure smectite (or illite/smectite with a high proportion of smectite), and a marked decrease of content of detritic material, together with the occurrence of zeolites and a significant decrease of the quartz/feldspar ratio are considered to be indicative products of submarine volcanic transformation (Pery et al. 1976; Lawrence et al. 1979). An association of smectite-biogenic opal, with extremely fine-grained smectite, may also indicate precipitation of smectites from solution. The source of the necessary elements may be precisely the dissolved (hydrated) volcanic material (ash), which is subject to rapid calcitization in a marine environment (Pery et al. 1976; Sturesson 1992). Therefore the absence of detritic minerals is also a criterion for assessment of the presence of volcanic material. K-feldspar, as one of the basic products of volcanic activity (Lawrence et al. 1979), is, or may be, a general source of K^+ for the creation of illites. However, a raised content of Fe is clearly limited by the origin of the volcanic material, as is the rate of sedimentation and the length of transport as well. According to Harder (1972), the content of Mg^{2+} in the environment, also plays a significant part. In our samples, we consider the high activity of Mg, which manifested itself in the mass formation of dolomites, to be a process occurring later than the hydratation and calcification of the volcanic material (Lintnerová 1988; Masaryk et al. 1993). Among the identified minerals, we consider the corrensites and illites (1M polytype) to be authigennous.

The corrensites are probably the most widespread group of mixed layered silicates (after the mixed layered illite/smectite minerals). They occur in the most varied geological environments (see the review Brigatti & Poppi 1984; Drits & Kossovskaya 1990). In the framework of the scheme of division of the corrensites into individual genetic groups (Drits & Kossovskaya 1990), we could divide our corrensites into sedimentary-diagenetic, connected with terrigennous- chemogennic evaporites, and carbonate formations. Kubler (1973) even identified an independent group of corrensites of carbonate formations. The presence of corrensites may also indicate the products of transformation of volcanic formations of an intermediate and basic character.

From the assumed composition of the volcanic material, and from the associations of minerals, which were identified in the clay fractions: illite, kaolinite, quartz and carbonates, it is not possible to consider the corrensite as a product of its transformation.

The mineralogical association completely lacked feldspar, which we expected would be present in volcanic formations (Pery et al. 1976; Lawrence et al. 1979). However in associations formed by the transformation of ash (Sturesson 1992), they were also not described. Zeolites, which often accompany corrensites from volcanic rocks (Kossovskaya & Drits 1975), were also not identified in the samples. Study of the residual fractions also brought no new information. Only ferrous sulphides, which are not specific, were identified. Occasional grains of apatite and zircon were previously described from the Turík

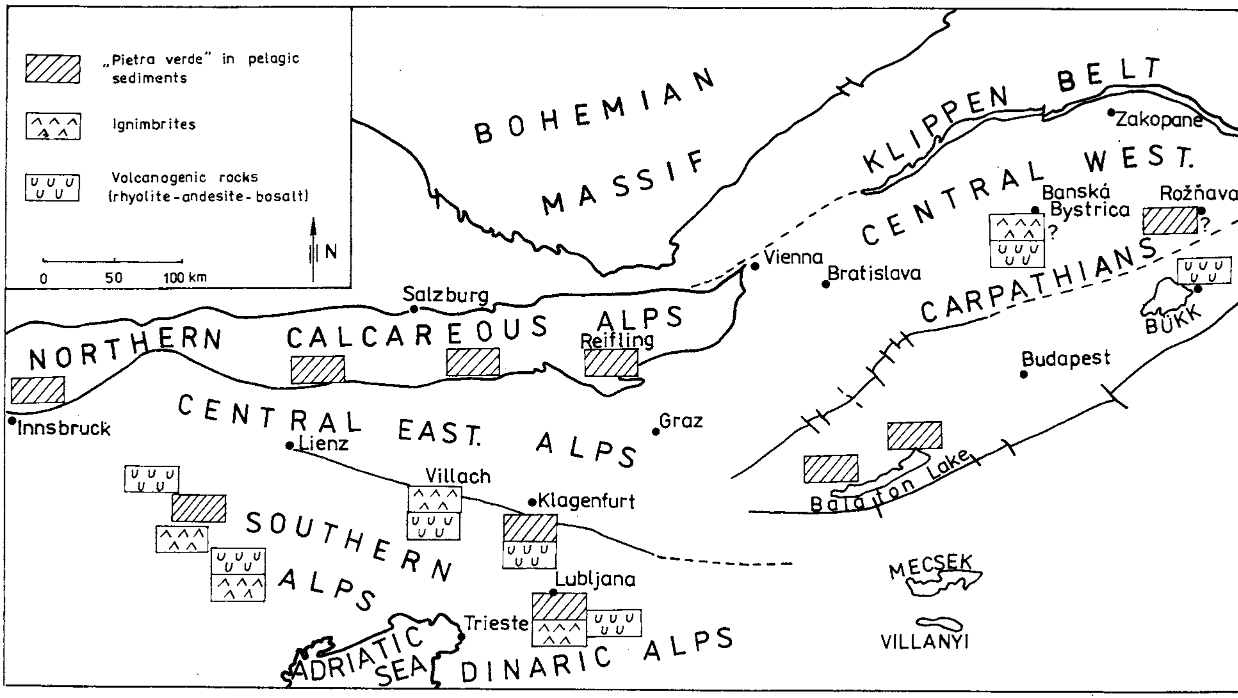

Fig. 4. The distribution of localities of the Middle Triassic tufites and volcanites in the area of the Eastern and Southern Alps and Western Carpathians.

profile (Havrila et al. 1988), but these are also frequent in the detritic Lunz Beds (Michalík et al. 1992).

An increased content of Fe was not found in the chemical analyses of the rock samples from the Turík profile (Havrila et al. 1988), or from the other profiles (Masaryk et al. 1993).

In relation to the individual determined parametres, we can consider the illite, identified in the individual samples, to be authigennous, and it probably did not originate by illitization of smectite. A detritic addition cannot be excluded with certainty, in relation to the mixing of two polytypes. Comparison with the clay minerals from the carbonate insoluble residue (IR) of the Reifling limestones (Lintnerová 1988; Masaryk et al. 1993; Lintnerová & Hladíková 1993) shows that the IR-illites were of detritic origin (accumulation on surfaces of pressure dissolution), and partly diagenetic, formed by illitization. We also assumed that smectites could be a source of magnesium for diagenetic dolomites, where they are associated exclusively with clayey layers (Masaryk et al. 1993; Michalík et al. 1992). The formation of authigennous carbonate minerals is also conditioned by the activity of CO_2 or HCO_3^-. The total dolomitization of the Reifling limestones is very intensive, and a specialized study of this problem has still not been done.

Summary

The identified clay minerals in the studied rocks, do not exclude the possibility of a volcanic admixture in these rocks. However, corrensite may also have a direct genetic connection with carbonate formations.

The Middle Triassic volcanic activities to the south of the sedimentary space of the Central Western Carpathians regularly influenced the sedimentary record of the hemipelagic and pelagic sediments of the Hronic Unit. Direct mineralogical indication of volcanic material has not been successfully proved. The increasing content of authigenic clay minerals, without direct relation to detritic minerals, is an indirect indicator of a volcanic contribution to the Reifling Depression. We consider that the sudden changes in the lithological record of the carbonate formations, and the slowing down of carbonate production on neighbouring carbonate platforms, may be a reflection of volcanic activity. The presence of volcanism in the southern zones also influenced sedimentation, causing the formation of extensive areas of cherty limestones. Enrichment of sea water with dissolved SiO_2 from volcanic products resulted in the development of siliceous plankton, mainly radiolarians.

Evidence of volcanic activity in the Middle Triassic are known along the whole northern margin of the Tethys Ocean (western part of the Southern Alps to Pamirs). They are a reflection of global changes, which were fully well-known in the Central Carpathian area in the Lower Jurassic, when a global reconstruction of a previously relatively simple sedimentary area occurred.

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