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Characteristics of Xenoliths in the East Slovakian Neogene Volcanites

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Abstract

The East Slovakian Neogene volcanic bodies contain mostly crustal xenoliths of various types. The chemical and mineral composition of the xenoliths, along with that of some enclaves, was studied through the use of CHA, XRD and EMPA. Xenoliths are rare in acid volcanic rocks, but abundant in intermediary andesites or basaltic andesites. The rhyodacites from the Zemplinicum tectonic Isle rarely contain magmatic enclaves with the features of argillitization, silicification and K-metasomatism. Extrusive andesite bodies in the Slanské vrchy Mts. are typical for xenoliths of sedimentary and metamorphic origin, but some magmatic enclaves were found as well. The pre-Tertiary Ca - skarnic xenoliths with boron-silicates (danburite, datolite) and cordierite hornfelses are also interesting.

Keywords: Neogene volcanites, magmatic enclave, xenolith, andesite, Slanské vrchy Mts., Zemplinicum Unit.

Introduction

The products of the East Slovakian volcanism that took place during the Neogene formed the Slanské vrchy Mts., the Vihorlatské vrchy Mts., and some volcanic bodies in the SE lowland area and around the Zemplinicum Unit, as well. They comprise calc-alkaline volcanic rocks, namely basaltic andesites, andesites, rhyodacites and rhyolites. These volcanic rock bodies, especially the basaltic andesite and extrusive andesite domes and lava flows, contain classic xenoliths and/or rounded enclaves.

Numerous papers have been devoted to the evolution of the East Slovakian Neogene volcanism (e.g. Kaličiak and Žec, 1995; Lexa and Konečný, 1998), but few have focused on the xenoliths of the area. The present article provides an overview of the various xenoliths found in East Slovakian Neogene volcanic rocks – mostly in the Slanské vrchy Mts. and around the Zemplínske vrchy Mts. (Fig. 1).

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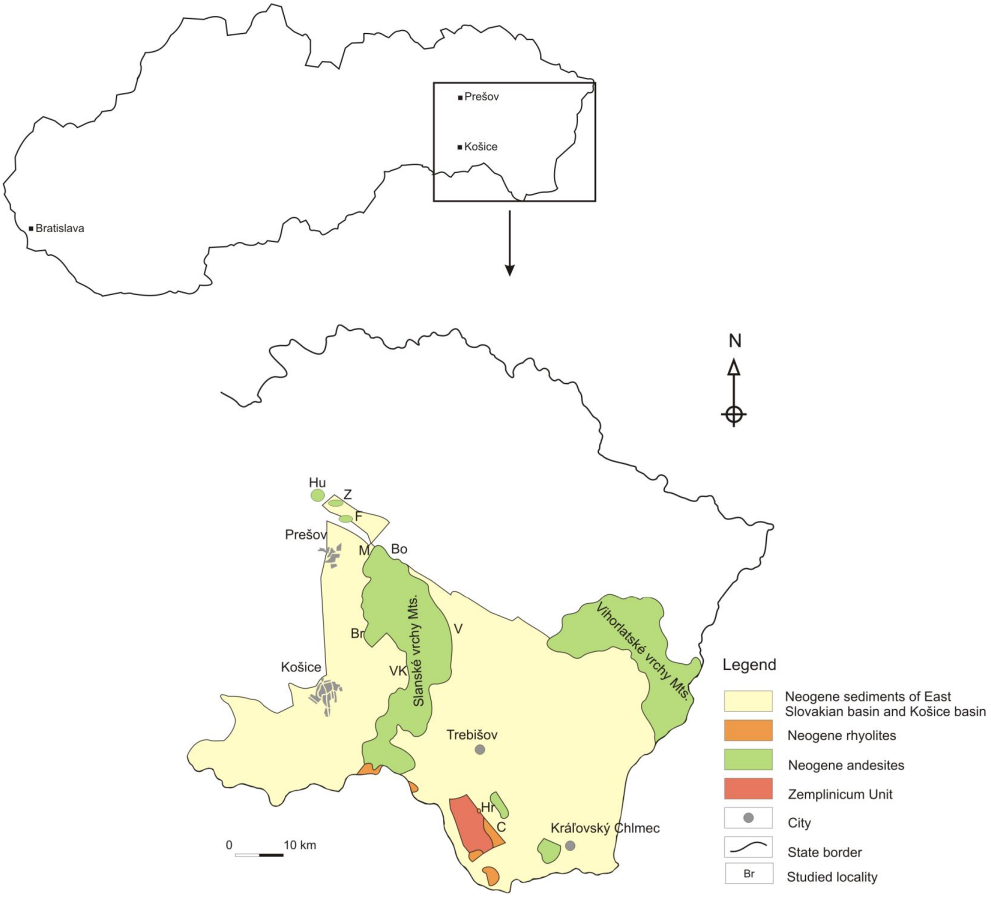

Fig. 1 Map of the East Slovakian Basin including Neogene volcanites and the studied localities (from Lexa et al., 2000). Abbreviations: Hu-Hubošovce, Z-Záhradné, F-Fintice, M-Maglovec, Bo-Borovník, Br-Brestov, V-Vechec, VK-Vyšná Kamenica, Hr-Hrčeľ, C-Cejkov.

Geological setting

The East Slovakian Neogene volcanites are situated within the East Slovakian Basin, filled by sediments of Eggenburgian to Pliocene age. Volcanism was first active in the NW section of the basin, followed by the Zemplínske vrchy Mts. area, where volcanic bodies of rhyolites, rhyodacites and andesites formed on the margins of the Zemplinicum tectonic Unit and in its vicinity (Kaličiak and Žec, 1995). The basement of these volcanic bodies is built by the sedimentary cover of the Zemplinicum Unit: upper Paleozoic sediments – sandstones, conglomerates, shales; Mesozoic sedimentary relics – sandstones, limestones, evaporites (in Baňacký et al., 1989). In this area, the volcanic activity started in the Lower Badenian and lasted up to the Late Sarmatian. In the Slanské vrchy Mts., the volcanic activity started in the Late Badenian, but the prevailing calc-alkaline products are of Sarmatian age. There, mostly composite volcanoes of andesite lava flows and their volcanoclastics were formed. The oldest units supposed to be found in the basement are the crystalline rocks of the Čierna Hora Mts.:

quartz-bearing gneisses, amphibolites, granodiorites, migmatites, Permian conglomerates, breccias, sandstones, shales and Mesozoic formations (Kaličiak et al., 1991). The youngest geological formation within the East Slovakian Basin is the Vihorlatské vrchy Mts. volcanic chain, formed by a range of small andesite composite volcanoes. Here, volcanics overlie older pre-Neogene units – the Humenné Mesozoic unit and Paleogene sediments.

Analytical methods

Thin sections were used in order to investigate the spatial distribution of minerals in xenoliths, in relation to the surrounding andesites. In order to determine the minerals forming the xenolith samples, X-ray powder diffraction was used, as well. XRD analyses were carried out by Mikrometa II at the Institute of Geosciences (Technical University of Košice). Microprobe analyses were performed in order to determine the chemical composition of individual minerals in xenoliths. A JEOL 6310 scanning electron microprobe with WDS or EDS belonging to the Institute of Mineralogy of the Karl-Franzens University in Graz, Austria, was used for this purpose. Measurements were carried out with a 10–15kV beam voltage, at an angle range of EDX 0–25° / WDX 0–30°. Mostly natural mineral standards were used for the quantitative calibration of element contents. The elementary composition of some homogeneous xenoliths was analyzed using classical chemical methods.

Petrography of host rocks and xenoliths/enclaves

Nearly all the samples coming from the volcanic bodies around the Zemplinicum tectonic Unit, as well as along the Slanské vrchy Mts., were collected from rock quarries. The quarries in Hrčeľ and Cejkov occur within the extrusive bodies of fine-grained rhyodacites.

a) Host rocks: light grey, compact, fine-grained **rhyodacites**. They are aphanitic rocks with sporadic up-to 1mm-large phenocrysts of plagioclase (Baňacký et al., 1989). The rock-forming minerals of the rhyodacite from Hrčeľ are K-feldspars (sanidine), quartz, goethite; sporadically, mica and plagioclase (albite) also occur. The host rock in the Cejkov locality is rhyodacite – white to yellowish, intensely silicified, very fine-grained. It consists mainly of quartz and K-feldspars (sanidine). Samples are frequently contaminated with Fe-oxides.

b) Enclaves with rounded shapes are relatively finer-grained rocks of grey colour, mostly 5cm in size. Their texture is porphyric with feldspar phenocrysts. About 50% of the mineral composition is comprised of quartz. Other major components are K-feldspars (sanidine) that predominate over plagioclase (albite to oligoclase). Clay minerals (kaolinite, illite), muscovite and goethite occur to a lesser extent. Tiny particles of marcasite are scattered within the enclaves of two samples from Hrčeľ. The contact points between the enclosed fragments and the host rock lack reaction coronas. This can indicate that, in contact with the colder rhyodacitic lava, the enclosed fragment underwent a rapid cooling process. The mineral composition of the enclave samples is summarized in Table 1.

Abundant xenolith occurrences are known in the Slanské vrchy Mts. Neogene volcanic rocks. Various types of xenoliths were enclosed especially in Sarmatian andesite extrusive bodies and shallow diorite-porphyrite intrusive bodies.

1a) Host rock: the light-grey to dark-blue **diorite-porphyrite** is compact, with a microcrystalline groundmass formed by over 50% plagioclase microlites. The minor or accessory phases are represented by pyroxene, magnetite, apatite and epidote. This type of rocks occurs in two of the studied localities – Borovník and Maglovec.

1b) The xenoliths comprise a wide range of rocks – volcanoclastics or even older sediments, dark biotitic rocks, and, in Maglovec, frequent enclosures with Ca-skarnic mineralization, up to

15–40cm in size. Colourful skarnic rocks with numerous cavities contain minerals such as wollastonite, hedenbergite, garnets, danburite, quartz, chlorite, calcite, zeolithes, and rare sulphides, as well.

Tab. 1 Mineral composition of enclave samples from volcanic bodies around the Zemplinicum tectonic Unit

Minerals	The Isle of Zemplin				
	Sample (enclave/xenolith)				
	XH-3	XC-3	XC-5	XC-6	XC-11
Qtz	x	x	x	x	x
Pl	x			x	x
Kfs	x	x	x	x	x
Ms		x	x	x	x
Lm (Gt)	x				x
Clay min.	x		x	x	x
Mrc (Py)	x				

XH - Hrčeľ, XC – Cejkov

2a) Host rock: the **pyroxene andesite** to **basaltic andesite** occuring in the Vyšná Kamenica and Vechec quarries are porphyric with pyroxene and plagioclase phenocrysts and hyalopilitic groundmass.

2b) In the locality of Vechec, frequent xenoliths of fine-grained grey-greenish tuffs and claystones were found (Kaličiak et al., 1991), filled by a younger hydrothermal minera-lization (calcite, tridimite, zeolithes). Enclosed in andesites, the dark bluish to black hornfels-like cordierite rocks, some spinel-bearing metamorphic rocks and partially molten enclosures with quartz were also found.

3a) Host rock: **hypersthene-amphibole andesites** occur in most of the localities studied – for example, in Fintice, Hubošovce and Záhradné. These belong to the Lysa Straž Complex, created by andesite extrusive and / or shallow intrusive diorite-porphyry bodies.

3b) Here, volcanosedimentary rock xenoliths coming from underlying basement units prevail. Less frequently, authigene magmatic enclaves were found as well, mainly in the Fintice quarry. The other rare type of enclosures is represented by dark hornfels-like fragments formed by cordierite, plagioclase and tiny andalusite. The most frequent are compact pelitic rock fragments, with sharp-edged crumbling. These mostly homogeneous xenoliths are almost light-grey or slightly greenish, in some cases with pink hues. The pink or reddish shade is the consequence of disseminated scales of secondary formed brown-red mica (biotite). The predominant minerals are plagioclase, pyroxene, hornblende, biotite, and magnetite. In some samples, ilmenite, chabazite and calcite can be observed. The xeno-liths from Hubošovce are rich in quartz. The bulk chemical composition of the assumed volcanosedimentary xenoliths is summarized in Table 2. The protholite of the xenoliths is believed to belong to: (1) the Teriakovce formation of Karpathian age, made up of greenish to grey siltstones and claystones; (2) the Eggenburgian Čelovce formation, represented by pale-grey siltstones to fine-grained sandstones. The present very fine pyroxene is a typical phase for volcanogeneous material. We assume it is evidence of the volcanosedimentary origin of the basement layers. The mineral compositions of the xenoliths from the Slanské vrchy Mts. are given in Table 3.

Discussion

The Neogene volcanites of the Slanské vrchy Mts. (+ the volcanic bodies around the Zemplinicum Unit) comprise predominantly andesites, basaltic andesites, their minor intru-sive rocks and also some random acid products (rhyodacites). Their extrusive bodies or lava flows, in particular, contain three main groups of enclosed rocks: magmatic enclaves of slightly more basic differentiates, common xenoliths of volcanosedimentary rocks and metamorphic rocks. In the third group we can also include the enclosures formed by skarnic assemblages, common only in the case of the Maglovec locality.

Magmatic differentiates

The typical features for this group of xenoliths are the similar texture and the mineral composition related to the host rock. The more basic chemistry of the enclaves determines the caustic effect range of entraining magma. According to Maury et al. (1978), magma has a minimal temperature effect on enclosed, more basic magmatic rocks because of the higher crystallization temperatures of their minerals. Here, enclaves of more basic magmatic rocks (with higher DI), captured in less basic moving magmas, create no reaction corona. Only structural changes can be noticed, including twinning-lamellae, undulosity, and cracks of their minerals. More acid enclaves in andesites are affected by desilication because of the component transition to the surrounding melt (Maury et al., 1978). On the other hand, the residual concentration of elements not integrated into the melt, such as Ti, Fe, Mn and Mg, is used to enrich the xenoliths.

All the chemically analysed samples of magmatic enclaves from the Slanske vrchy Mts. are more basic. Their SiO_2 contents: 56,8% - FX1, 54,5% - VX5, 44,9% - HX6 and 41,9% - BrX2 are approximately smaller at about 7%, 2%, 16%, and 18% than in the host andesites (Fig. 2). The desilication of xenoliths mentioned by Maury asserted in this case only minimally. In sample FX1, montmorillonite generated as a consequence of xenolith alteration. Other authigene enclosures – BrX and HX (without CHA) – contain only pyro-xene or plagioclase crystals, rarely biotite – locally cumulated along the contact points (as a temperature effect of andesite).

Sedimentary rocks and micaceous metamorphic rocks

The most frequent group of xenoliths found in andesites of the Slanske vrchy Mts. con-sists of fragments of Neogene and Paleogene basement sedimentary formations. This xenolith group comprises mostly plagioclase, pyroxene, minor quartz and clay minerals. Phases typical for host effusive rocks dominate here, as well. We can confidently expect the obvious metasomatic effects of magma in izochemical xenoliths. Only a slight affect by mafic minerals was noticed.

Metamorphic xenoliths are generally rich in aluminous and Fe-Mg phases, where the following may differ: 1) residual phases rich in Al-minerals (Al_2SiO_5, Al-garnets, cordierite and felsic mica); 2) products of mica breakdown; 3) recrystallization phases such as felds-pars, biotite, pyroxenes and amphiboles, with a chemistry similar to that of the surrounding lava.

Most of the xenoliths found in the Slanské vrchy Mts. belong to the group with a more basic chemical composition and lower levels of the alkali elements Na + K than is typical for common sedimentary rocks (Fig. 3). However, they are rather distant from the schist or pelite composition field. Most of them are poorer in Fe and Mg contents than is typical for pyroxene and amphibole-bearing hornfelses (Fig. 4).

Acid fragments from crystalline complexes (gneisses, mica schists etc.) are not obvious at the sites studied. Acid metamorphics under higher temperature conditions typical for basaltic andesite lavas have a tendency to melt with the formation of vitreous rhyolitic reac-tion coronas (not occurred in xenoliths). It modifies the original components of individual parts of xenoliths, but the bulk chemistry remains unaltered (Maury et al., 1978). Higher SiO_2 contents are noticeable only in the clastic xenoliths ZX3 and ZX4 from Záhradné, whose protholite we can rather assign to the Paleogene or Neogene sediments. We assume relatively basic protholites for the dark grey xenoliths BoX5, KX2 and VX2. The sample VX2 from Vechec, with its vitreous corona, represents a fragment of an area where partial melting was taking place. The molten parts can contain recrystallized minerals such as sani-dine, tridimite, cordierite or orthopyroxene (Grapes, 1986). In these samples, cordierite is the remarkable mineral. Under low pressure conditions (0,5–4kbar), cordierite can form at a wide range of temperatures (Winkler, 1976), its more endothermic, ferruginous varieties forming at 900°C (Deer et al., 1992). The cordierites described from the regional metamorphic rocks of Veľká Fatra and the Western Tatras crystalline complex (Slovakia) (Janák and Kohút, 1996; Ludhová and Janák, 1999) originated at higher pressures (4–5kbar) and a temperature of 600 – 750°C, through the following reactions: sillimanite + garnet + quartz, or sillimanite + biotite + quartz. This mineral association fairly differs from the xenoliths of Borovník, Vechec and Vyšná Kamenica, where cordierite is present in para-genesis:

BoX5: + magnetite + plagioclase;
VX2: + plagioclase + melt + ilmenite (+ younger Na-stilbite);
KX2: + plagioclase + Fe-spinel +/- amphibole (+ younger biotite + quartz).

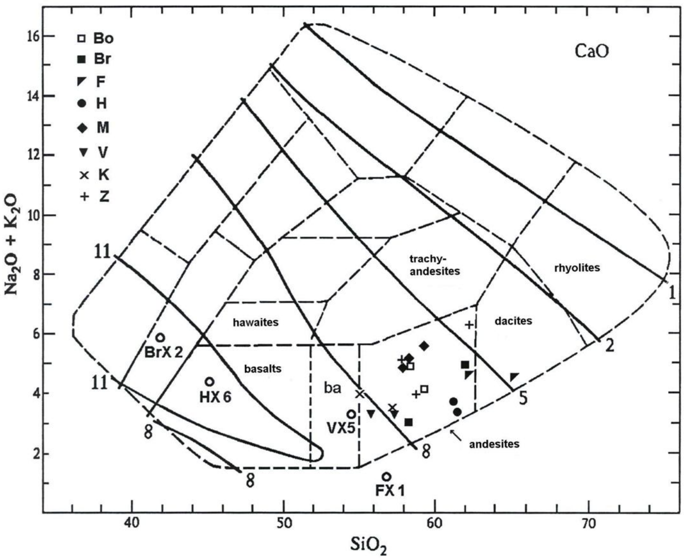

Fig. 2 The bulk chemical composition of host rocks from 8 localities along the Slanské vrchy Mts., including 4 magmatic enclaves (Košuth, 1999, according to Cox et al., 1993; crossing solid lines mean CaO content).

Cordierite within the samples from the Slanské vrchy Mts. has more likely originated from rocks with a higher Al content, through crystallization from the partially molten protholite (Košuth, 1999).

Another type found in andesites of the Slanské vrchy Mts are micaceous xenoliths. Some samples (BrX1, BrX2, BoX2, MX3, and MX6) predominantly contain dark mica. We can interpret the origin of the essential biotite content and its balanced distribution in xeno-liths as the effects of the andesite temperature, leading to amphibole-rich rock alteration. The textural features of the samples from Brestov point to a glimmerite precursor.

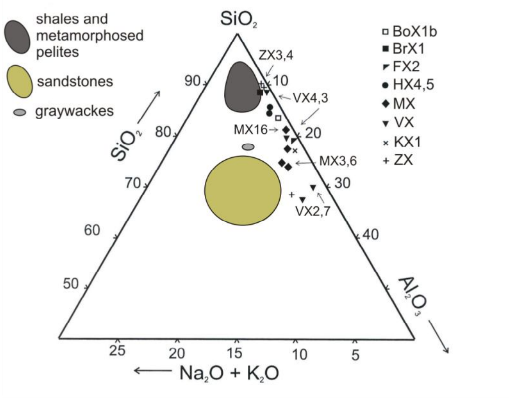

Fig. 3 Ternary diagram for the relations of SiO_2–Al_2O_3 vs (Na_2O+K_2O) in xenoliths from the Slanské vrchy Mts.

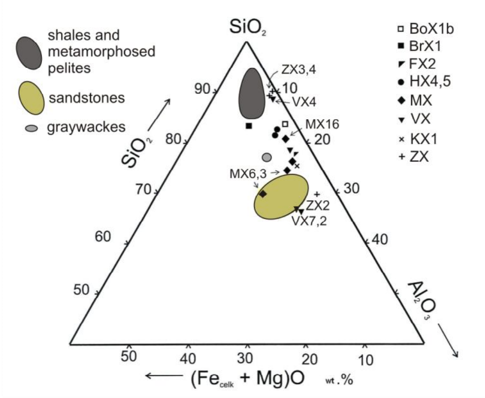

Fig. 4 Ternary diagram for the relations of SiO_2–Al_2O_3 vs. (Fe + Mg)O in xenoliths from the Slanské vrchy Mts.

Pre-Tertiary skarn xenoliths

The low stability of the major mineral – calcite – was essential for the conditions of the metamorphosis of carbonates by the contiguous magmatic body. Wollastonite originated from calcite in the xenoliths within the basement of the Maglovec locality. The origination of wollastonite at the expense of calcite is irreversible, and it confirms a typical acicular habitus and, often, quartz remaining in skarn products. The reaction with SiO_2 took place at temperatures higher than 400°C, through the diffusion on calcite of Si, Ca and O ions found in a solid state, and a system open for CO_2 migration (Suk, 1979). Wollastonite has not been generated either during the low-pressure metamorphosis (400–500°C), or during con-tact metamorphosis at very shallow depth; here, we assume the formation of Ca-skarn at the level of the magmatic chamber. For the skarn xenoliths from Maglovec, the presence of yellow to brown garnet – grossular $Ca_3Al_2[SiO_4]_3$ – is typical, but Fe andradite is also noted. Within the sample MX1, grossular creates a relatively thin corona only around the andradite-bearing core, without the obvious progressive trend of Mg enrichment towards the rims. Andradite is a typical high-pressure product of caustic metamorphosis, forming under a wide range of pressures, of up to 20kbar (Hinz, 1970). The following reaction can be considered as the relevant equation of origin:

$$3CaCO_3 + \text{(magma) } Fe_2O_3 + SiO_2 \rightarrow Ca_3Fe_2[SiO_4]_3 + 3CO_2$$

The extraordinary feature of the Ca-skarn xenoliths from Maglovec is the conspicuous abundance of danburite and datolite borosilicates. In this assemblage, datolite is stable in relation to danburite when the H_3BO_3 activity is low; its increase in activity as a result of an increase in temperature leads to the crystallization of danburite. The prevailing occurrences of danburite in all the MX samples correspond to temperatures of 550–600°C at a pH<6, including the abundance of quartz (Yang and Rosenberg, 1995). Minimal chemical changes of solidified minerals would manifest during the short-time contact with magma, as des-cribed in the case of carbonate xenoliths from Highland County, Virginia (Mitchel and Freeland, 1986). We assume that, within the Maglovec xenolith assemblage, such extensive changes must be performed on the long term, with the participation of some boron-bearing liquid solutions leaking from the upper volcanosedimentary rocks with evaporite horizons.

Conclusions

The Neogene volcanites of East Slovakia contain various types of xenoliths. Within the samples from Hrčeľ and Cejkov (Zemplinicum tectonic Isle), the mineral composition of the enclosed fragments is consistent with host rhyodacite. It suggests that these are likely magmatic enclaves, not xenoliths belonging to the older subjacent formations. The clay minerals contained in the samples (mostly from Cejkov) can be an evidence of argillitization. In these samples, silicification and K-metasomatism can also be observed (Baňacký et al., 1989).

Tab. 2 Whole rock chemical composition of sedimentary xenoliths from Hubošovce, Záhradné and Fintice

Locality	Hubošovce		Záhradné			Fintice
Xenolith sample	HX4	HX5	ZX2	ZX3	ZX4	FX2
SiO_2	56.67	57.04	49.5	79.00	72.00	53.58
TiO_2			1.00	0.00		
Al_2O_3	15.54	14.52	28.8	9.17	10.19	20.90
Fe_2O_3	5.00	5.57	8.50	0.53	1.39	2.98
P_2O_5	0.00	0.00		0.02		
FeO	5.45	3.88	0.28	1.14	4.59	4.29
MnO	0.08		0.03	0.03		
CaO	7.68	7.45	0.84	6.72	7.29	14.46
MgO	3.95	4.11	1.20	1.20	2.21	0.96
K_2O	2.80	2.20	5.60	0.48	0.19	0.40
Na_2O	1.20	1.00	1.80	0.53	1.19	0.40
H_2O^-	0.31	1.51	0.56	0.10	0.20	0.62
H_2O^+	1.21	3.00	2.63	0.85	0.90	1.08
Sum	99.81	100.28	99.81	99.76	100.15	99.58

Enclaves contain rare acid volcanites such as dacites and rhyolites, but they are abun-dant in andesites and microdiorites; their presence depends on the petrographic type of the host rock (Nitoi et al., 2002). As mentioned above, the fragments enclosed in the Neogene volcanites of the Slanské vrchy Mts. represent three main groups of rocks: Tertiary volcano-sedimentary rocks of the direct basement, pre-Tertiary metamorphic and metaso-matic rocks, and magmatic enclaves. The interpretation of the xenolith fragment bodies relevant to the tectonic complexes of the basement derived from the comparison of the petrographic features of the xenoliths to those of the potential rocks of volcanite basement formations. The relevance of xenoliths for the Neogene volcanosedimentary formations can be evidenced by the bulk chemical analysis and mineralogical composition, correlating xenoliths with the host rock.

The temperature imprints observed at the exocontacts of the xenoliths are minimal, with a thin reaction corona and a minimum of newly-generated phases. Apparently, the assumed temperature of andesitic magma – about 800–900°C – is not sufficient for these processes during short-time interaction. The xenoliths from Maglovec are extraordinary in the region because of their various skarnic mineral associations. We assume they were formed from marly limestones, under depth conditions, more than 5km conforming the magmatic chamber level. The widespread metasomatic changes could signify the contact with upper parts of the chamber body during the long-term effects of mobile magmatic fluids enriched by migrating fluids originating from the marine evaporite layers. The alte-ration observed at the contact zones of the xenoliths is mostly minimal. Often, it is masked by later postvolcanic processes such as limonitization, silicification and zeolitization.

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Tab. 3 Mineral composition of xenolith / enclave samples from Slanské vrchy Mts.

Minerals	Slanské vrchy Mts.											
	Sample (enclave/xenolith)											
	BoX1	BoX3	BrX1 BrX2	BrX3 BrX4	BrX5	BrX7	FX1	FX2	FX4	FX5 FX6	FX7	FHX1
Qtz	x					x	x	x	x	x	x	
Pl		x	x	x	x	x	x	x		x		x
Kfs			x									
Cpx		x		x	x	x		x	x	x		x
Bt			x		x							
Ms	x										x	
Phl												x
Ilm				x								
Cal												
Mag								x				
Lm (Gt)	x											
Clay m.	x					x	x				x	
Chl			x									
Am												
Zeol												x
Trd		x										
Mrc (Py)												
Stb			x									
Crd												
Grt												
Wo												
Dat												
Danb												
Hd												
Anl												
Cbz									x			x

Tab. 3 (continued)

	HX4	HX6 HX8	MX1	MX4	MX5	MX6	VX2	VX3	KX4	ZX1	ZX2	ZX4
Qtz	x								x	x		x
Pl		x	x		x	x	x	x		x	x	x
Kfs												
Cpx		x			x			x		x		
Bt	x	x			x	x			x	x	x	x
Ms												
Phl												
Ilm							x					
Cal				x	x				x		x	
Mag										x	x	x
Lm (Gt)									x		x	
Clay m.									x			
Chl						x						
Am	x			x		x						x
Zeol												
Trd												
Mrc (Py)							x	x				
Stb							x					
Crd							x					
Grt		x	x	x								
Wo			x		x							
Dat			x									
Danb			x	x	x							
Hd												
Anl				x	x							
Cbz	x											

BoX - Borovník, BrX - Brestov, FX - Fintice, HX - Hubošovce, MX - Maglovec, VX - Vechec, KX - Vyšná Kamenica, ZX - Záhradné

enclaves | skarns | volcano-sedimentary xenoliths | metamorphic xenoliths

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