Auxiliary sciences in archaeology, preservation of relicts and environmental engineering.
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DARK MINUTE NODULES IN ANDESITE FROM THE FINTICE QUARRIES (EASTERN SLOVAKIA), ITS CHARACTER AND POSSIBLE ORIGIN

Drobne ciemne koncentracje w andezytach z kamieniołomu w Finticach (Wschodnia Słowacja), ich charakter i prawdopodobne pochodzenie

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Abstract

Crystals of pyroxene, plagioclase and ilmenite, present at andesite from Fintice, Eastern Slovakia – were examined using the traditional chemical analysis, polarizing light microscopy, scanning electron microscopy with EDS detector and Raman spectroscopy. Special attention was paid to geochemical determination of rockforming phases crystal growth and to stages of its crystallization. Obtained data were used for reconstruction of these phases crystallization i.e. phases of alternation because of magma chemistry.

Key words: spotty andesite, extrusive bodies, dark enclaves,

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Introduction

Fintice is at present a place of intensive andesite exploitation in two stone quarries. This locality (Fig. 1) is geologically well-known because of wide range of enclosed xenoliths and enclaves, up to 20÷30 cm large), but also because of frequent zeolithe mineralization occurrences, filling the wall rock fissures (Košuth, 2000; Marcinčáková-Košuth, 2011). Along with the study of xenolithes, local spotty character of surrounded light grey andesite was observed.

There were found tiny oval nodules of grey to black-grey colour, evenly diffused in pale andesite host-rock from both Fintice quarries. The aim of this work is to describe these nodules (assemblage of crystals) and search their composition, using the combination of light microscopy, SEM as well as Raman spectroscopy. Resembling to rounded magmatic enclave, but more or less regularly distributed in enclosing andesite it was supposed to be the fine relics of magma-mixing and evolution.

Geographical setting and geology of the area

Andesite extrusive bodies create morphologically distinct group of volcanic hills and elevations, NE from the town Prešov (*Fig. 1 a, b, c*). The samples location, both andesite quarries by Fintice belongs to tectonically exposed Kapušany horst and the Stráže group, which include also several larger volcanic hills. In space-time distribution of Neogene volcanic formations this complex of bodies belongs to the wider Lysá Stráž - Oblik complex, which is lineary arranged in the NW-SE direction, and partly rim the Slanske vrchy Mts. The Slanske vrchy form morphologically distinct volcanic range, spreading from the central area of Eastern Slovakia, southward to the Hungarian border. It represents the inner Carpathian volcanic arc, composed of Neogene calc-alkaline products, forming mostly composite volcanoes with less share of extrusive bodies (Kaličiak-Žec, 1995).

The wider terrain is the NW border part of East-Slovakian Neogene basin, filled by sediments of main molasses phase (of Eggenburgian-Karpath age) with thin Quaternary sediments cover. Proximately close to the north they are delimited by Čelovská depression (Kaličiak et al, 1991). The local WNW – ESE graben structure spread approximately 16 x 6 km between Záhradné and Slivnik. The depression was terminated by faults of NW – SW direction – some along the Klippen belt – and younger transversal faults SW – NE direction, which terminated the block segmentation.

Morphologically striking complex of volcanite bodies around Fintice overrun the composite horst evolution and can be subdivided into two units. West of the road Zahradne-Fintice uprise a group of a few dome-shaped extrusive bodies of hornblende-pyroxene andesite, or of augite - enstatite (hyperstene) andesite with hornblende. Among them the most impressive are Straž (740 m), Lysa Straž cones; and too; here also belong the flat Hôrky body, lobe Maliniak body and separately situated conus of the Šariš hill, formed by pyroxene andesite with minor garnet. Andesite bodies have irregular elliptic basis with lateral WNW - ESE prolongation. East of mentioned local road extends more coherent Kapušany horst. It is built by the pyroxene andesite of same *Sarmatian age,* although westward of Fintice also an older remnants of rhyolitic tuffs horizon are registered. The longitudial horst is volcanic ridge, tectonically steeply shaped, particularly against the Prešov depression on its southern edge (Kaličiak et al., 1991). According to Buday in Matějka at al. (1964) and Leško-Slávik (1967), along the horst axis was developed even the older Paleogene anticline zone, called Kapušianske pasmo belt. The south-eastern elongation of the Kapušany volcanic horst can comprise the shallow laccolite bodies (*Mid-Samatian age*, 12,0±0,5 Ma), especially the exposed Maglovec laccolite of diorite-porfyrite on the northernest margin of Slanske vrchy Mts range (Kaličiak-Repčok, 1987). **Błąd! Nie można odnaleźć źródła odwołania.**

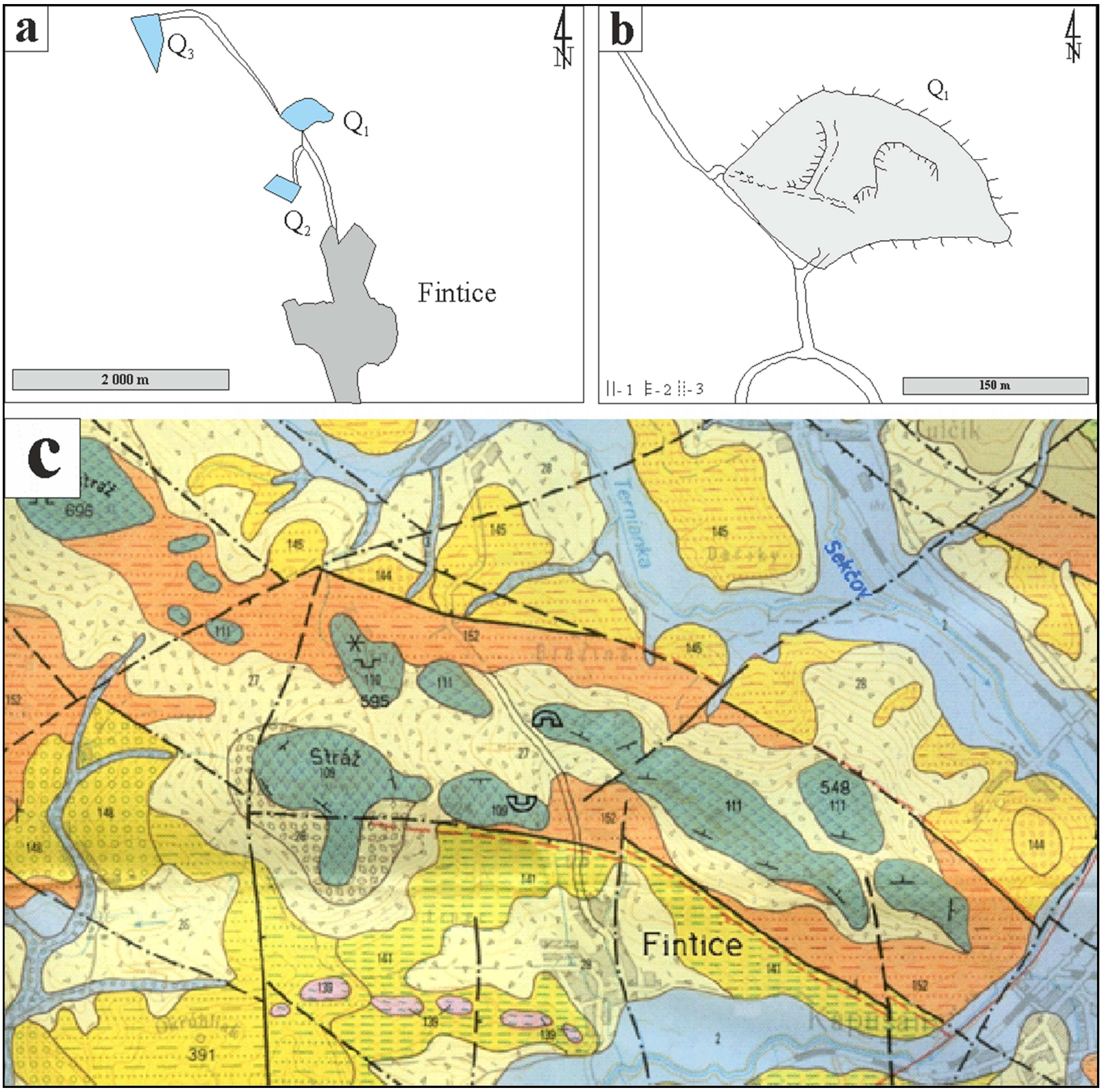

Fig. 1. Maps showing locality of quarries near Fintice. **a** - an andesite quarries (Q_1-Q_3); **b** - location of andesite quarry where have been found described samples; **c** - Geological map of the Kapušany group of volcanite extrusive bodies with the position of Fintice vilage and quarries Q_1 and Q_2 (by Kaličiak et al, 1991, adapted) .

Legend to geological map of the Kapušany group of volcanite extrusive bodies with the position of Fintice quarries and vilage:

No. 26: gravity sediments, stony block fields; **No. 27** and **No. 28**: slope and deluvial sediments, mostly loam-stony, Quaternary; **No. 109**: extrusions of augite-hypersthene andesite with amph., mid.Sarmatian; **No. 110**: extrusions of pyroxene-amphibole andesite with garnet, mid.Sarmatian; **No. 111**: extrusions to laccoliths of hypersthene-amphibole andesite, mid.Sarmatian; **No. 139**: rhyolite tuffs and epiclasic sandstones with volcanic admixture, Karpatian; **No. 144** and **No. 148**: light-grey to brown sandstones with conglomerates, Eggenburgian; **No. 145**: light-grey siltstones to fine-sandstones, Eggenburgian; **No. 152**: flysch sandstones, siltstones, claystones with intraformational conglomerates, Paleogene.

Character of studied samples

Andesite rock material was sampled in both Fintice quarry. The repertoire of all samples of light grey pyroxene andesite with random amphibole included that with a few and tiny (0,2 cm) disseminated dark oval spots to samples similar to left one in *Photo 1*, with dense concentration of spot groups up to 0,5 cm in diameter. Distinctly darker spots by its oval shape resemble to minute enclaves of darker grey to black-grey colour, without glassy or any lustrous surface. Locally its linear /elongated aggregation event. greyish veinlets can be seen. The cut fields of these nodules enclose euhedral pyroxene porphyroblasts, same as plagioclase, so its grey interior is not homogeneous (*Photo. 1, 2a*). Some cases the contour of spots is not oval, but angular to polyhedral, it resemble to cross-section of garnet tetragon three-octahedron crystal shape (*Photo. 2b*).

Photo 1. *Cut and original fragments of spotty andesite. Natural size of the middle sample is 7x3 cm; (scanned by M.Košuth)*

Methods of investigation

Mineralogical investigations were realised using the optical microscopic study, SEM with EDS detector and Raman spectroscopy too.

Optical methods comprised analyses of magnified scanned pictures, rough samples microscopy (by Zeiss Technical 2) and thin section – polarizing light microscopy (by A70 – China production). Study of spots in thin sections under polarised light showed specific plagioclase zonality, as well as specific structures of pyroxenes. On the other hand the intergrown pyroxene brown porphyroblasts were confirmed.

Scanning electron microscopy analyses were performed on FEI Quanta SEM, model 200 FEG. These analyses were expanded to the research of chemical composition in the microarea. They were made using the EDS detector. The samples were coated with carbon prior to analyses. The study was conducted in the "High Vacuum" mode; accelerating voltage was 15 kV.

Raman spectroscopy was done using the DXR Raman Microscope, made by Thermo Scientific Co. Obtained spectra were compared with an internal minerals database, provided by the manufacturer of the microscope.

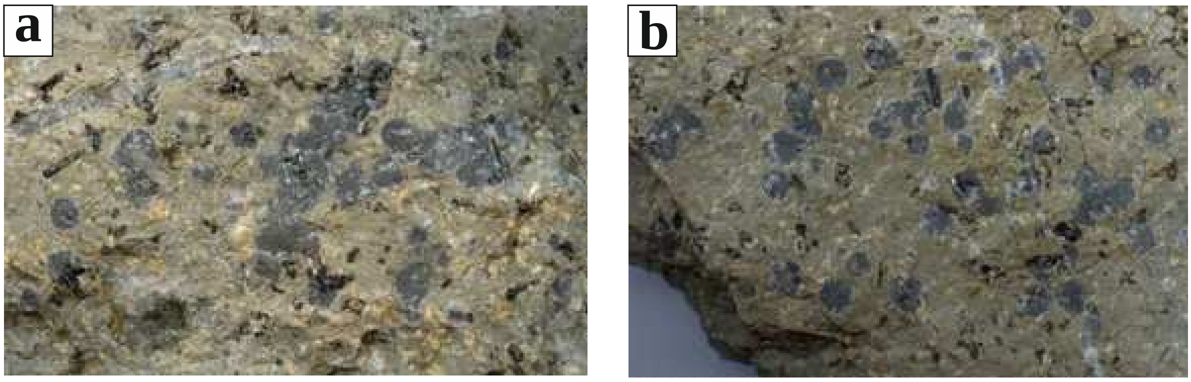

Photo 2. a - Linear group of spots and also younger fissure filling (left-up part) in detailed view; real frame wide 4,2 cm. **b** – Semi-angular contours of some nodules resemble to garnet tetragon three-octahedron; frame wide 5,3 cm; (scanned by Košuth).

Results of the nodules study

It could bring the explanation : first pyroxene and plagioclase crystallization, the next shaped garnet crystals were partially resorbed by magma glassy rest, later forming the undifferentiated andesite base matter.

To such a development could indicate the special type is pyroxene-hornblende andesite (Tab. 1) with random garnet, which forms in Šarišský Castle extrusive body and the close Maliniak body respectively. The presence of garnet however is the extraordinary feature. Garnet – in average mostly of almandine composition (by Brousse et al., 1972: $Pyr_{10,2-17,9}$ $Alm_{57,9-60,9}$ $Spes_{6,0-7,3}$ $Gros_{4,7-15,2}$ $Andr_{9,1-12,8}$. It forms dark-redish rounded grains of the size 0,5 to 1,2 cm in the diameter, irregularly distributed in andesite.

The other type of enclosures are some hornfelses fragments; the diferent type are magmatic enclaves, occur mainly in the Fintice quarry. Most relevant to studied nodules could be the oval magmatic enclaves of slightly brownish colors, composed of predominant plagioclase forming its pilotaxitic structure with some quartz and montmorilonite admixture (Košuth, 2000). Its bulk rock chemical composition represent the analysis of FX-1 sample in Tab.1. Xenoliths of various types, occured in Fintice and Hubošovce are accompanied by common zeolithes of fissure type. Because of its presence – drussy of zeolithe crystals with younger calcite – the range of contact magma imprint is mostly not obvious.

Tab. 1.
Chemical composition of andesite rock and the magmatic enclave FX-1 from the Fintice (weight %)

locality	Fintice		enclave
sample	1	2	FX-1
SiO_2	65,49	62,29	56,80
TiO_2	0,41	0,53	traces
Al_2O_3	16,81	17,94	20,26
Fe_2O_3	4,89	1,51	3,91
P_2O_5	0,16	0,18	traces
FeO	—	3,01	3,27
MnO	0,11	0,03	traces
CaO	5,14	6,12	7,40
MgO	1,83	2,41	2,50
K_2O	1,75	1,71	0,40
Na_2O	2,86	2,85	0,66
H_2O-	0,35	0,35	1,84
H_2O+	0,68	1,24	2,48
SUM	100,48	100,17	99,51

Results of mineralogical investigation

✓ Plagioclases (bytowinite - anorthite)

Microscopic observation carried out at polarized light showed complicated structure of plagioclases (Photo 3). Most of crystals is of zonal structure (Photo 3a, b). Twinning are not typical and suggest the crystals were cracked and next at these places plagioclase had crystalized again, but it shows completely other direction of growing as well as directions of optical axes. Moreover are observed inclusions of opaque minerals, mostly near centre of crystals.

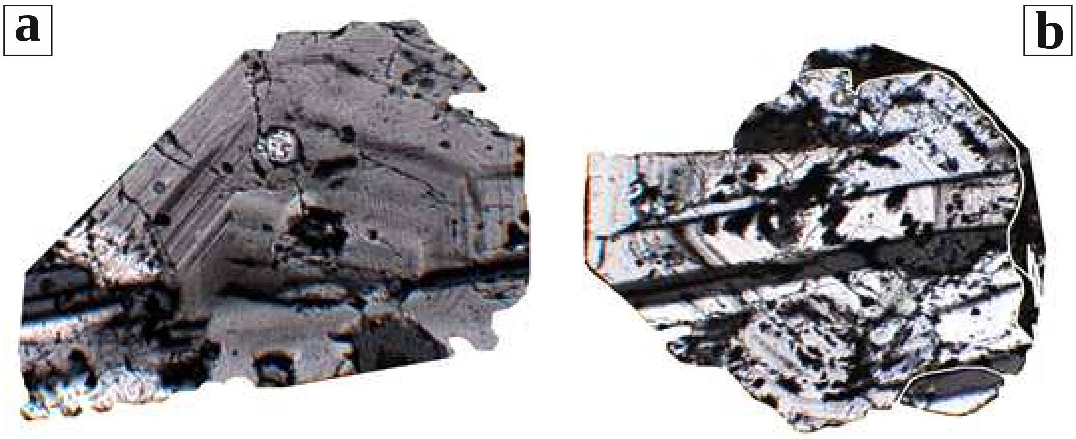

Photo 3. a, b - crystals of plagioclases (anorthite) showing zonal structure, not typical twinning and inclusions. Polarized light, magnification 45 x.

Examination of plagioclases using EDS methods confirmed chemical zonality of crystals observed earlier at polarized light. Results (Tab. 2) document, that central part contain more Ca what means that magma at early stages of crystallization of these plagioclases showed other more alkaline composition then at next phases of crystallization where at crystals one can notice higher sodium concentration. Observed phenomenon suggest modifying of magma during crystallization of plagioclases, starting from magma containing more calcium to slightly less basic magma, containing more sodium. This evolution was the result of Ca absorption in crystalizing plagioclases and relative higher concentration of Na in magma.

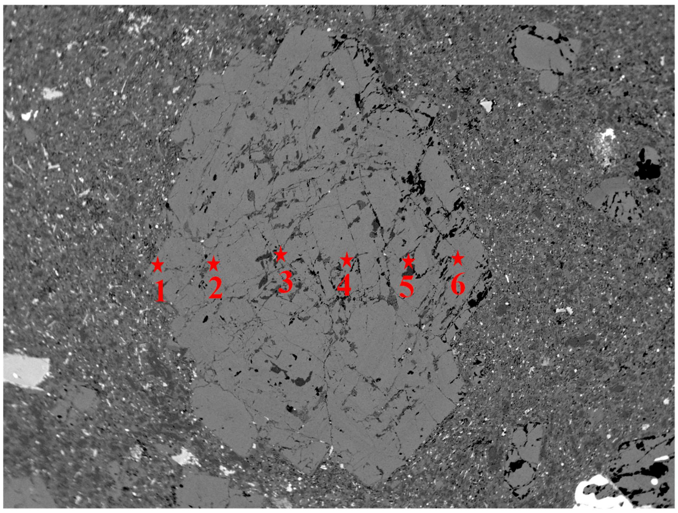

Photo 4. Microphotograph showing places of chemical analysis of zonal plagioclase, incorporated to next tab. 2. magnification 55 x.

Tab. 2

Tab. 2. Selected results of plagioclase point EDS analyses (Photo 4)

Point	***Na_2O***	***K_2O***	***FeO***	***SiO_2***	***CaO***	***Al_2O_3***
1	2,60	0,10	0,16	49,42	15,05	32,61
2	1,75	0,09	0,13	47,11	16,80	34,07
3	1,52	0,07	0,15	46,43	17,20	34,62
4	1,62	0,01	0,10	46,92	17,10	34,16
5	0,04	0,13	0,11	50,98	15,56	33,13
6	2,51	0,10	0,14	48,74	15,54	32,89

Obtained data were used for classification of plagioclases (fig. 2)

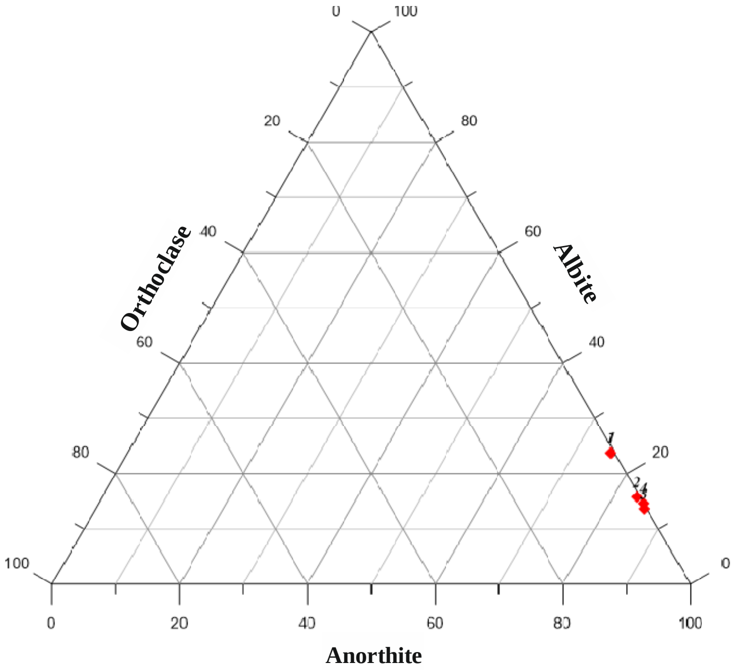

Fig. 2 Triangle of feldspar classification. Red points - results of chemical point analyses from Fintice.

Results of chemical analyses were confirmed also by Raman spectroscopy (Fig. 3).

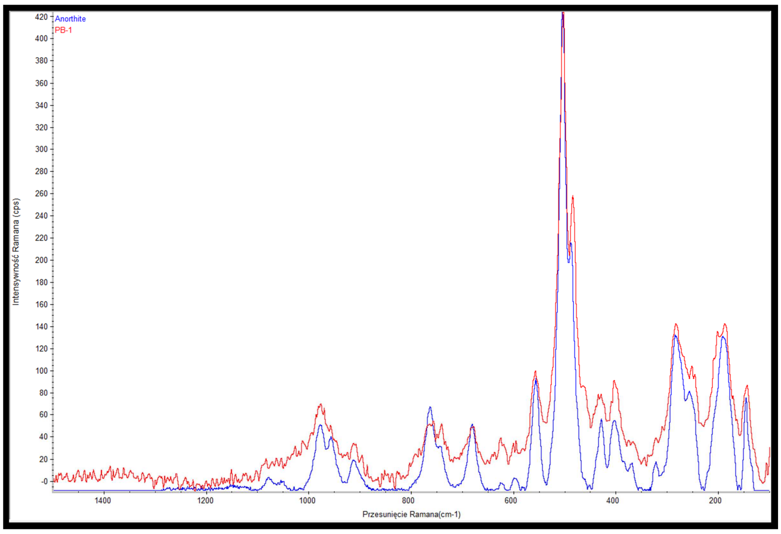

Fig. 3. Raman spectra of central part of plagioclase (anorthite) phenocrystal. Red spectra –investigated crystal, blue - standrad spectra of anorthite.

- ✓ **Pyroxene I (ferrosillite - hypersthene)**

Observations of pyroxenes performed by the use of polarizing light microscopy confirmed – as typical for the andesites - the presence of two types of these minerals.

First one, slightly more frequent in andesite is represented by crystals with inclusions of many opaque minerals, represented mostly by magnetite (Photo 5a). These crystals show characteristic twining structure at polarized light (Photo 5b). One can observe the twining is typical rather for plagioclase then for pyroxene. This type of twining seen as various optical orientation of subcrystals document changes of directions of pyroxene growth during its crystallization.

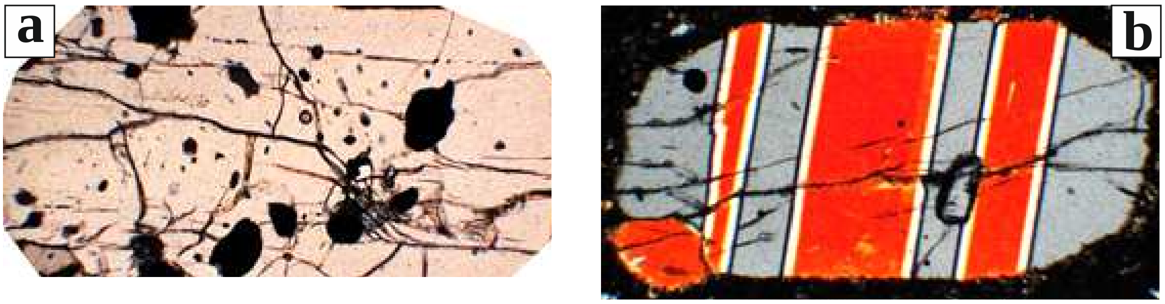

Photo 5. Pyroxene of first type. A –inclusions of magnetite at structure of ferrosillite. B – twining at crystal of ferrosillite. a – 1 polaroide , b - X polaroides. Magnification 45 X.

Chemical analyses performed using the EDS method document zonal structure of pyroxenes and different content of Fe, Mg, Mn, Ti as well as Ca and Si at various parts of one crystal (Photo 6, Tab. 3)

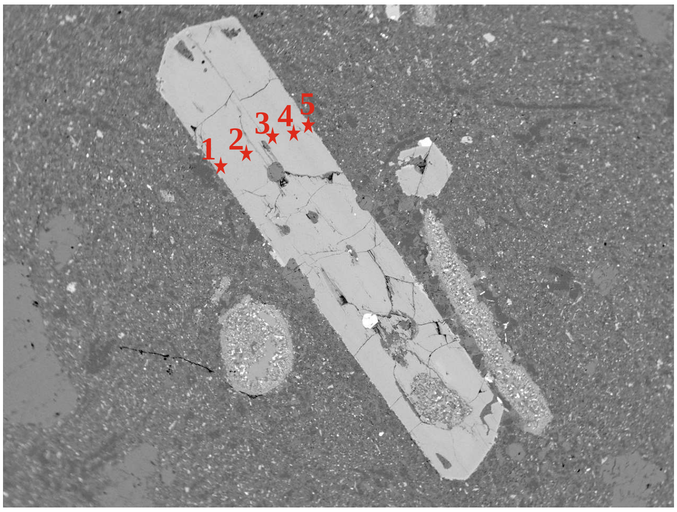

Photo 6. Example of examined pyroxene crystal.
Red points – places of chemical analyses; magnification 45 X

Tab. 3. Selected EDS results of pyroxene (Ferrosillite) (points from the Photo 6).

Point	*TiO_2*	*MnO*	*FeO*	*NiO*	*SiO_2*	*CaO*	*Al_2O_3*	*MgO*
1	0,14	0,55	23,55	0,05	51,64	1,19	1,24	18,17
2	0,18	0,61	25,12	0,11	51,56	1,00	1,37	18,24
3	0,10	0,65	24,90	0,02	50,92	0,88	1,39	17,51
4	0,14	0,60	24,72	0,01	50,90	0,92	1,40	18,25
5	0,12	0,66	24,89	0,05	52,13	0,85	1,00	18,22

Location of obtained data of chemical examination confirms this type of pyroxene represent ferrosillite (Fig. 4, variety hypersthene).

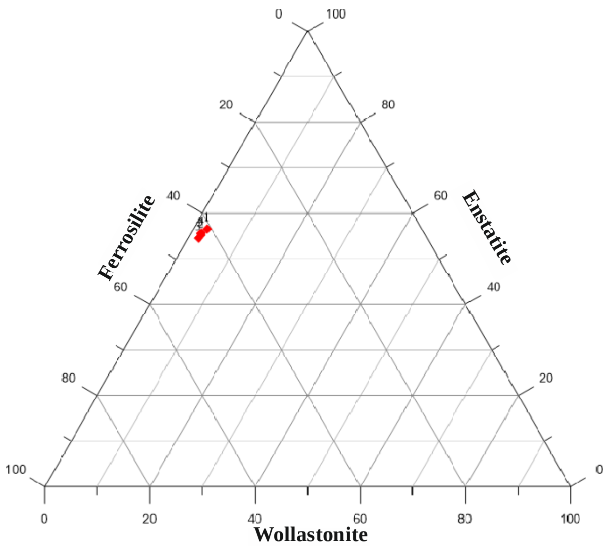

Fig. 4. Triangle of pyroxene classification with marked red points of our analyses, incorporated to Tab. 3

- ✓ **Pyroxene II**

Second, more rare type of pyroxene is seen under microscope as crystals surrounded with thick dark zone composed of opaque minerals. These crystals are aggregated as a striking reaction rim and sometime contain opaque inclusions (Photo 7 a, b)

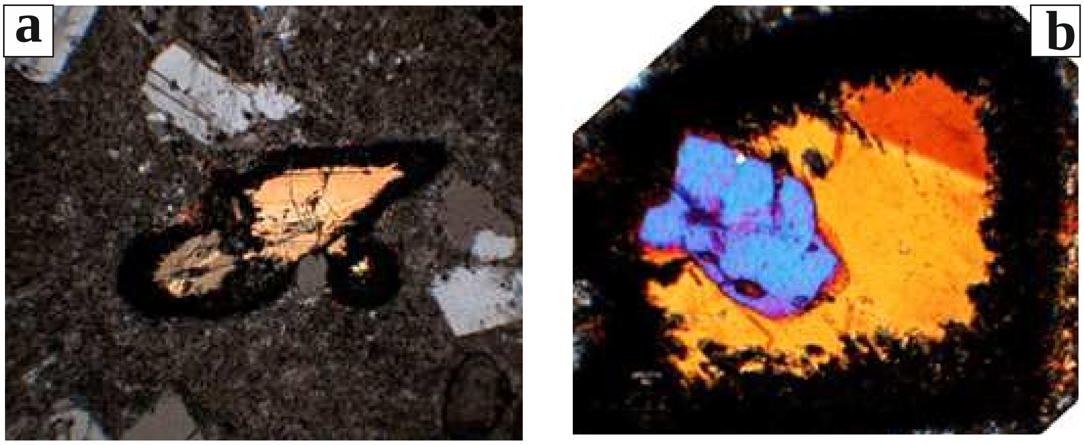

Photo 7. Pyroxenes of second type. **a** – concretion of two crystals of pyroxene. Polarized light, paralel polaroids; **b –** X polaroids, magnification 80 x

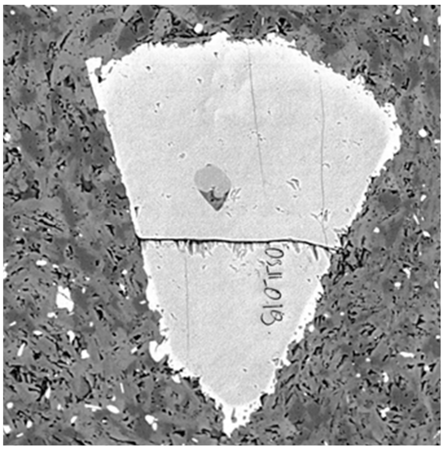

Photo 8. SEM microphotograph of examined pyroxene II from andesite mass, magnification 120 x.

Central part of crystals contain high amount of calcium, while amount of Fe is relative low. Observed optical features as well as results of chemical analyses suggest that pyroxenes under consideration (Tab. 4, internal points) belong to isomorphic quadrilateral Di-Hd-En-Fs serie of Ca-pyroxene close to diopside, with main components approx. formula:

(2-int) $Ca_{0,78}Mg_{0,73}Fe_{0,37}Si_{2,002}O_6$ (3-int) $Ca_{0,801}Mg_{0,72}Fe_{0,38}Si_{1,99}O_6$

Tab. 4. Selected results of pyroxenes EDS point analyses (Photo 8).

Point	*Na_2O*	*SiO_2*	*MnO*	*FeO*	*NiO*	*CaO*	*TiO_2*	*MgO*	*Al_2O_3*
1 – external	0,03	51,67	0,98	31,77	0,02	1,53	0,10	13,19	0,50
2 – internal	0,15	54,04	0,35	11,83	0,03	19,86	0,30	13,22	1,33
3 – internal	0,17	53,74	0,45	12,09	0,03	20,19	0,30	13,05	1,38

- ✓ **Ilmenite**

Frequent accessory component at examined andesite is ilmenite. It is present as separate opaque crystals at main rock mass as well as constitute inclusions in crystals (mostly in pyroxene). Crystals of ilmenite are of irregular shape (Photo 9).

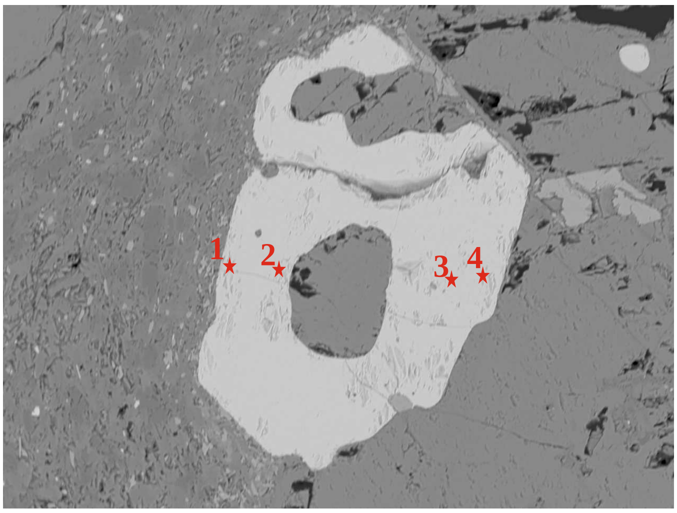

Photo 9. Irregular crystal of ilmenite situated at the contact of feldspar and andesite mass. Red points show places of chemical examination.

Chemical analyses of ilmenite document tab. 5 and confirm oscillation mostly of Fe and Ti. Additionally examination conform presence of interesting admixtures of vanadium. These concentrations makes ilmenite from Fintice interesting raw material for possible separation of this element.

Tab. 5. Selected results of ilmenite point EDS analyses (positions seen in Photo 9).

Point	*FeO*	*MnO*	*TiO_2*	*V_2O_3*	*MgO*
1	42,83	0,48	49,27	6,29	0,82
2	42,28	0,58	49,57	6,30	1,01
3	43,43	0,49	49,05	6,27	0,66
4	42,78	0,45	49,43	6,29	0,83

Conclusions

Carried out examination documents variations of structure and chemical composition of phenocrystals, present at andesite from Fintice. These variations reflect changes of chemical composition of magma during the crystallization of plagioclases, both types of pyroxenes as well as ilmenite. Mentioned oscillations of magma chemistry lead to changes of directions of crystallization of phenocrystals, observed just within the plagioclase and pyroxene crystals as its twining and sectorial multi-twining.

Examination additionally shoved high content of vanadium at crystals of ilmenite.

Literature

Brousse, R., Bizonard, H. et Šalát, J.: 1972: Grenats des andezites et rhyolites de Slovaquie. Origine des grenats dans les series andesitiques. Contr.Miner.Petrol., 201-213, Berlin.

Kaličiak, M., Baňacký, V., Jacko, S., Janočko, J., Karoli, S., Molnár, J., Petro, Ľ., Syčev, V., Škvarka, L., Vozár, J., Zlinská, A. and Žec, B., 1991: Geological map of Slanske vrchy Mts. and Košicka kotlina depression - Northern part, 1: 50 000; and Explanation to geological map of Slanske vrchy Mts. State Geological Institute of Dionysus Štúr, 1-229 p. Bratislava (*in Slovak*).

Kaličiak, M. and Repčok, I. 1987: Reconstruction of the time development of volcanoes in the Northern part of Slanske vrchy Mts. Mineralia Slovaca, Vol.19, 401-415. Bratislava (*in Slovak*).

Kaličiak, M. and Žec, B. 1995: Review of Neogene volcanism of Eastern Slovakia. Acta Vulcanologica, Vol.7, (2), 87-95; Pisa-Roma.

Košuth, M., 2000: Mineral composition of xenoliths from the Fintice andesite quarry. Mineralia Slovaca, Vol.32, 3, 237-240; Bratislava.

Leško, B. and Slávik, J., 1967: Le trais fondamentaus de la structure géologicque de la région entre les Karpates occidentalles and Karpates orientales. Geolog. Zbornik, 18, 1, 169-172, SAV, Bratislava (*in Slovak*).

Marcinčáková, Z. and Košuth, M., 2011: Characteristics of xenoliths in the East-Slovakian volcanites. Analele Stiintifice ale Universitatii Al.I.Cuza - Geologie, Vol.(Tome) 57, Issue 1, 17-27, Iasi, Romania.

Matějka, A. et al., 1964: Explanation to comprendious geological map of ČSSR 1: 200 000; M-34-XII, M-34-XXVII Zborov-Košice. Central Geol.Institute, Prague (*in Czech*).