

## Zoned clinopyroxenes from Miocene basanite, Banská Štiavnica – Kalvária (Central Slovakia): Indicators of complex magma evolution

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**Abstract.** The basanite neck Banská Štiavnica - Kalvária ( $7.29 \pm 0.41$  Ma) belongs to the oldest alkaline basalt eruptive centres from the inner side of the Western Carpathians. This basanite has porphyric texture with olivine, clinopyroxene and plagioclase phenocrysts. Zonation is the characteristic feature of clinopyroxenes. There are some kinds of the zonation: core (centre) - mantle - rim, concentric, sector and oscillatory zoning. Ti-diopsides and Ti-augites of sandy and dark brown color, which constitute centres, mantles and rims of phenocrysts, come from alkaline basalt magma which was not differentiated to the high degree. The variability of Ti and Al contents suggests polybaric crystallization - inner parts of clinopyroxenes with lower Ti contents formed at higher pressures than rim parts with higher Ti contents. The oscillatory zoning of these pyroxenes can reflect changing conditions in the melt. The core corresponding to Cr-augite was found in one of the samples. This Cr-augite can represent fragments of the upper mantle wall rocks which were caught by ascending basaltic magma. The green cores of type I. (ferrian aluminian diopsides and augites) originated in a melt or they come from the vein fillings in the upper mantle. Their origin from the magma melt could be suggested from the zoning and subhedral shape of some cores. Mg-number and variability of the chemical composition of these cores can reflect more differentiated magmas with a variable degree of differentiation. Their origin as fillings of the upper mantle vein systems could be suggested by the cores with shapes resembling fragments. The higher  $Al^{VI}/Al^{IV}$  ratios comparable with those of clinopyroxene mantles suggest crystallization of these cores at relatively high pressure. Strongly resorbed cores of type II. (Fe-rich diopsides and augites) are probably xenocrysts which come from the upper mantle metasomatized by rising melts and fluids. It is also possible that some cores of this type originated in more differentiated magma (e. g. zoned subhedral core). Studied clinopyroxenes show the complexity of processes which accompany alkaline basalt magma evolution and its interaction with the subcontinental mantle.

**Key words:** alkaline basalts, zoned clinopyroxenes

### Introduction

Alkaline basalts are an important source of the information about the upper mantle but also about lower parts of the Earth's crust. These information we can obtain, when we study these rocks, because they originate by partial melting of the upper mantle materials and because of their rapid rise from the asthenospheric depths they are little contaminated or almost not contaminated by the crustal material. They contain xenoliths which represent fragments of wall rock material taken to the surface by the magma.

Pyroxenes, the common minerals in basalts, are the worthy source of information about the evolution of alkaline basalt magma to their ascent up to the surface, about its interaction with mantle, respectively crustal wall rock material and the other magmatic melts. Their wide compositional variability is influenced not only by the composition of the material (magma) which they originated from, but also by P, T conditions of their origin.

Clinopyroxenes in Miocene-Quaternary alkaline basalts from the Western Carpathians were more detaily

studied only in one of two regions of alkaline basalt occurrence, in Novohrad (Nógrád) region, which lies at the boundary between Slovakia and Hungary (Dobosi, 1989; Dobosi and Fodor, 1992; Dobosi and Jenner, 1999). The aim of this work is the similar study in the second area, Central Slovak volcanic field, more exactly at the locality Banská Štiavnica - Kalvária.

### Geology

The locality Banská Štiavnica - Kalvária (Fig. 1) is one of the several occurrences of alkaline basalts in the Štiavnické vrchy Mts. area. It represents the lava neck formed by nepheline basanite in the surrounding of amphibole-biotite andesite. This neck represented conduit of probably smaller explosive-effusive volcano which was successively eroded (Konečný et al., 1998).

Radiometric age of basanite  $7.29 \pm 0.41$  Ma (Balogh et al., 1981) corresponds to the Upper Miocene (Pontian) and to the oldest stage of alkaline volcanic activity in the inner side of the Western Carpathians.

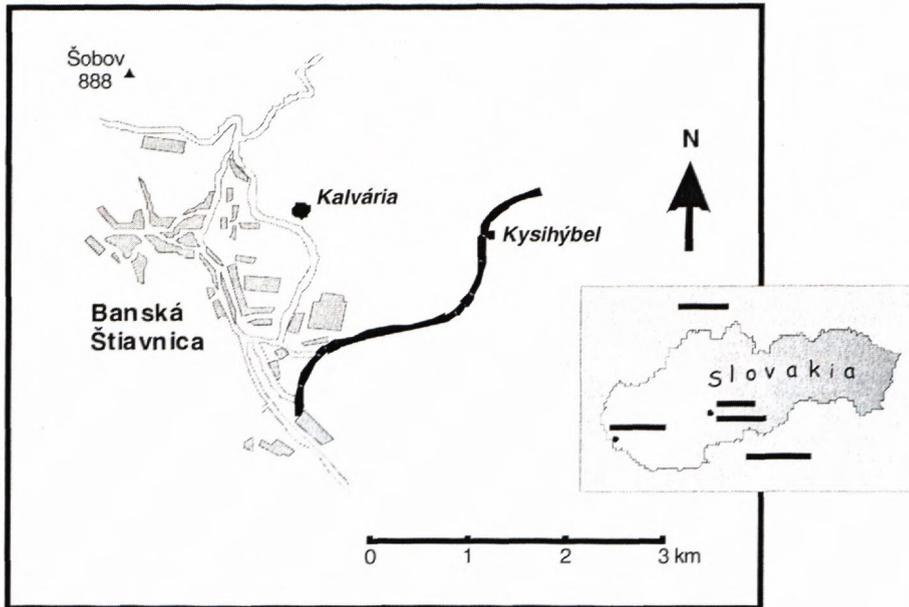


Fig. 1 Two occurrences of alkaline basalt (Kalvária and Kysihýbel) near Banská Štiavnica city

### Petrography and mineralogy

The *basanite* from Banská Štiavnica, the locality Kalvária, forms more petrographic types. It has porphyric holocrystalline, more rarely hemicrystalline texture with omnidirectional, ophitic or trachytic groundmass (Fig. 2). Phenocrysts are represented by olivine, clinopyroxene and plagioclase. The matrix consists of these minerals, Ti-magnetite, nepheline, apatite and respectively, of glass (Šímová, 1965).

*Olivines* are euhedral to anhedral; phenocrysts often have large size (also some mm). They are also present in the groundmass. Starting alteration (e. g. iddingsitization) follows cracks. Olivines contain inclusions of Cr-spinel. They are often zoned, the zonation is visible also optically. Their composition is approximately  $Fo_{80-88}$  (central parts) and  $Fo_{73-77}$  (rims). According this composition, these olivines are phenocrysts which have crystallized from basalt magma.

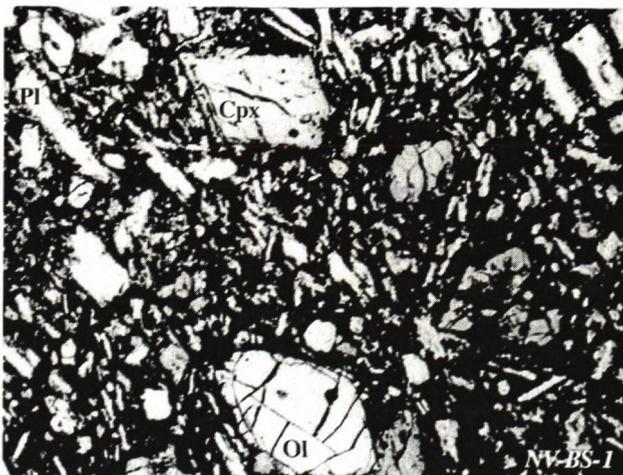


Fig. 2 Alkaline basalt from Banská Štiavnica – Kalvária. Plane-polarized light, magnification 27x. Ol – olivine, Cpx – clinopyroxene, Pl – plagioclase

*Clinopyroxenes* form euhedral to anhedral phenocrysts and groundmass grains. Phenocrysts are relatively often rounded and embayed. Clinopyroxenes are typically zoned (core, mantle and rim zone, concentric, sector and oscillatory zoning).

*Plagioclases* form tables and laths, predominantly in the groundmass. They are omnidirectional, ophitic or fluidal. They are characteristically twinned. Phenocrysts are generally non-zoned or weakly zoned with composition  $An_{74-84}$  (Balogh et al., 1981). Analyzed plagioclase xenocryst probably of the crustal origin has the inner part of  $An_{43}$  composition. It is rimmed by the another plagioclase with  $An_{69}$ .

Inner parts of some clinopyroxene crystals are to the various scale replaced by *secondary carbonates* (photo 3, 4, 5, 7). Secondary carbonates with zeolites also fill interstices in the rock.

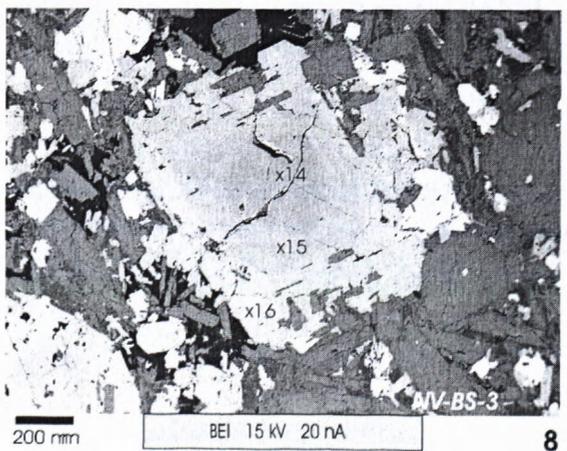
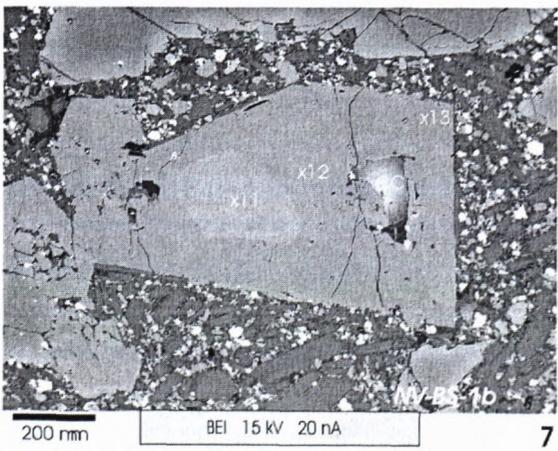
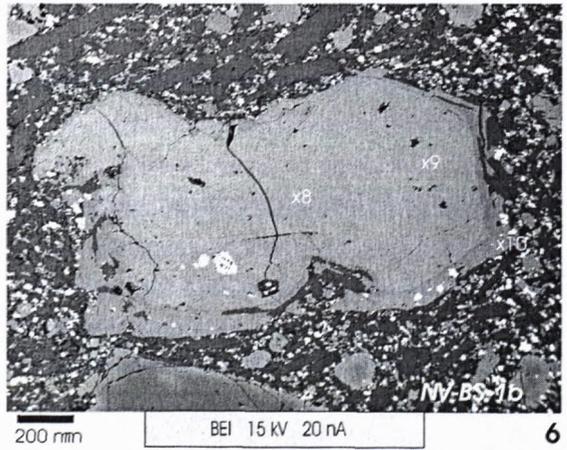
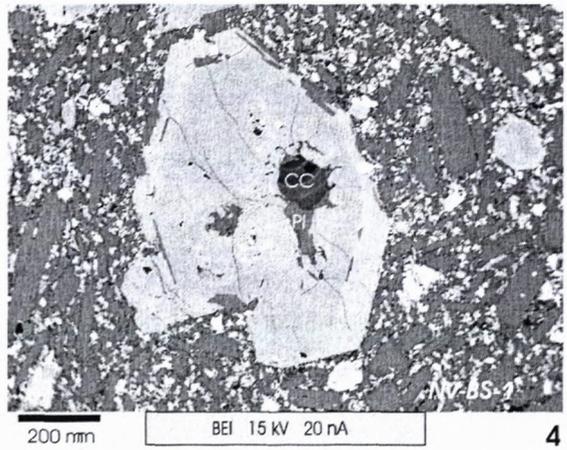
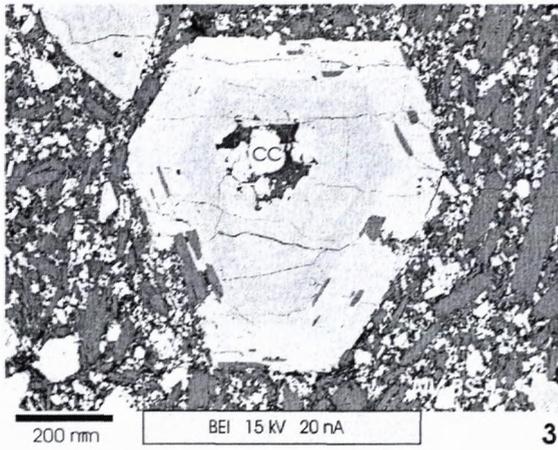
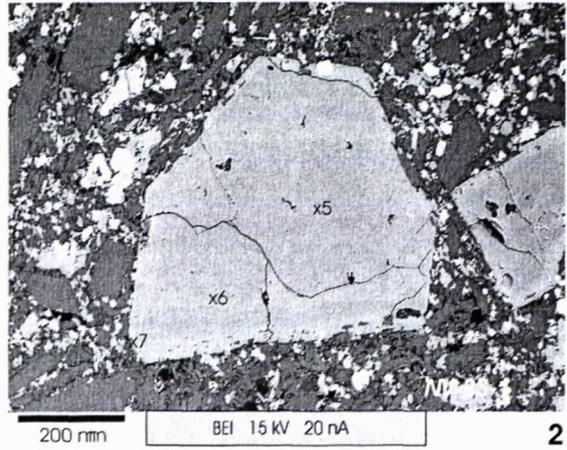
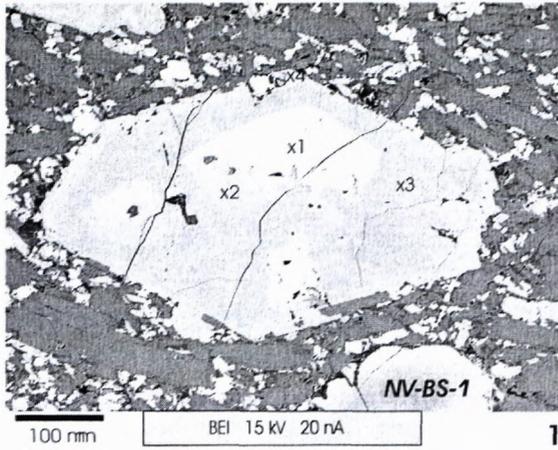
### Geochemistry

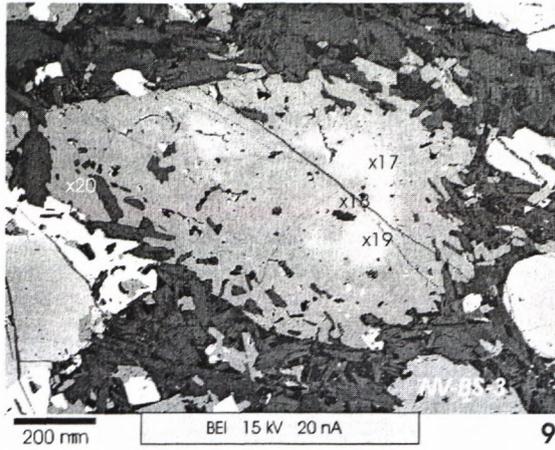
Geochemistry of basanite from Kalvária together with the another alkaline basalts from the Central and Southern Slovakia was described by Miháliková and Šímová (1989), more recently by Ivan and Hovorka (1993). According Ivan and Hovorka (1993) this rock belongs to alkaline withinplate basalts with their characteristics features: LILE and HFSE enrichment and differentiated enrichment LREE/HREE.

If we compare this basanite with most of the Miocene to Pleistocene Western Carpathian alkaline basalts, this rock as a product of the oldest eruption phase has mildly lowered total abundances of REE and some other incompatible elements such as Th, Zr, Ta.

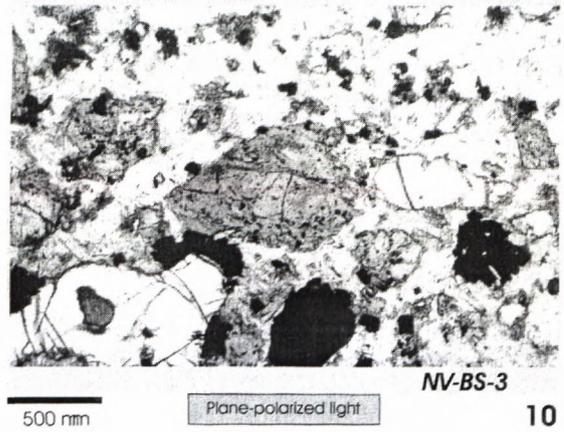
### Analytical techniques

Pyroxenes were analyzed at Cameca SX-100 electron microprobe at Geological Survey of Slovak Republic, Bratislava. An accelerating potential of 15 kV, current 20 nA.

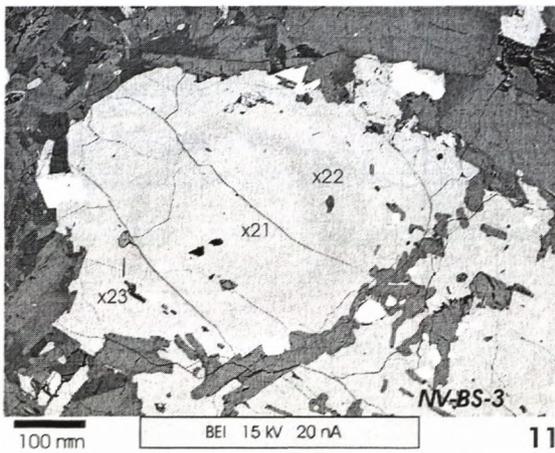




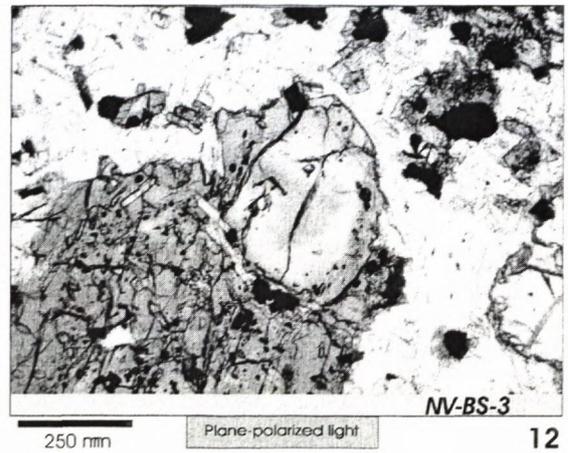
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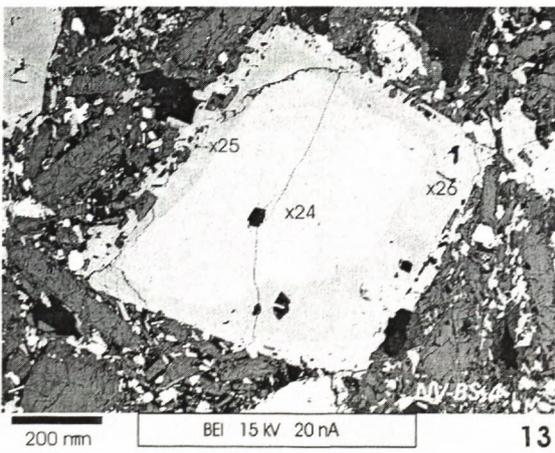
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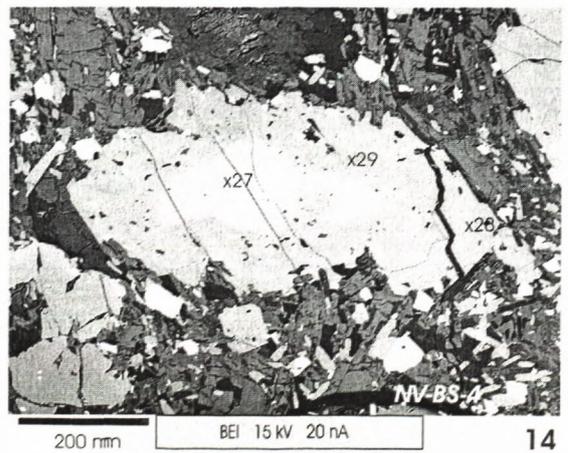
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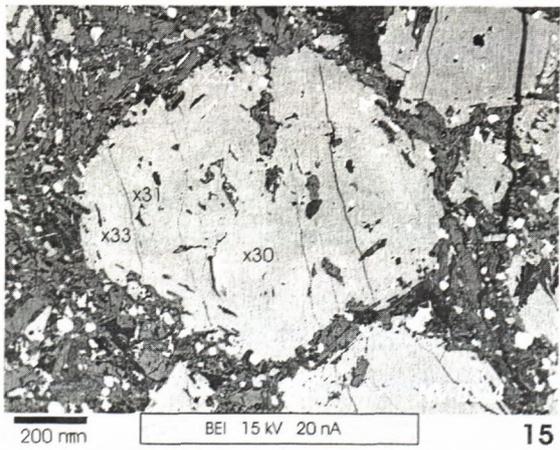
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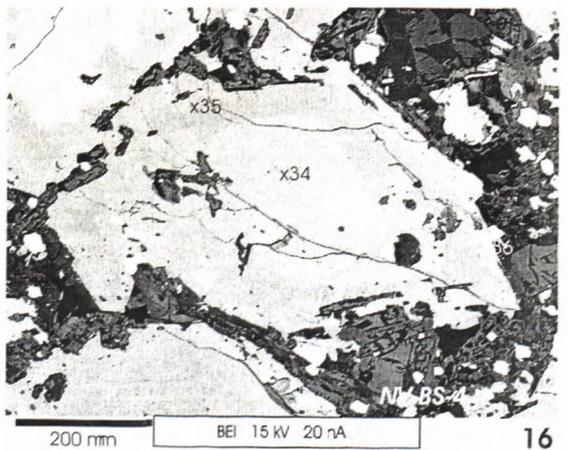
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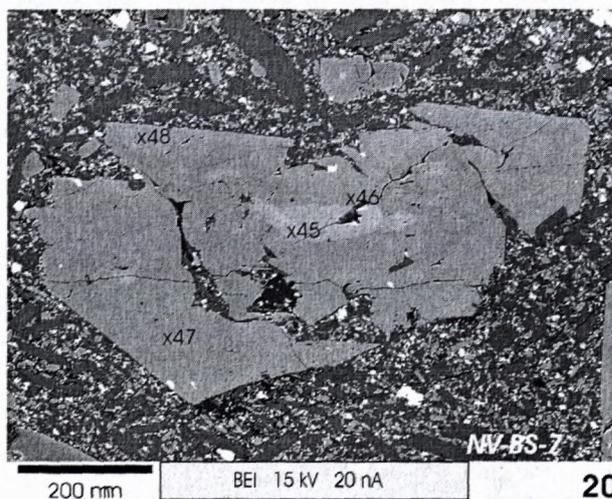
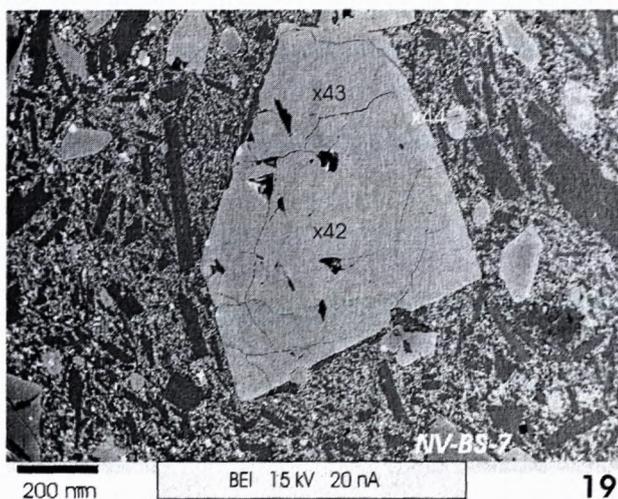
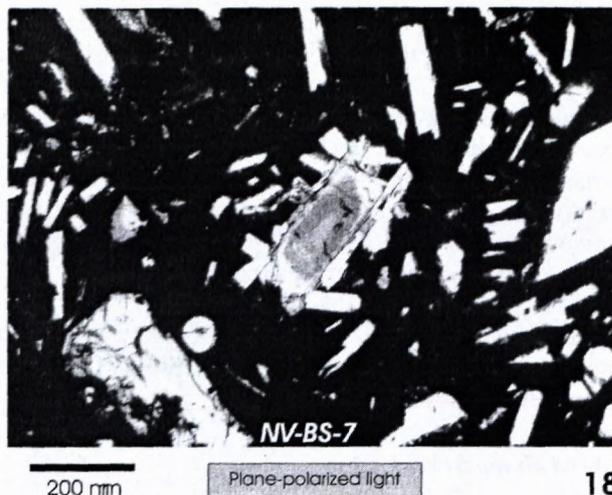
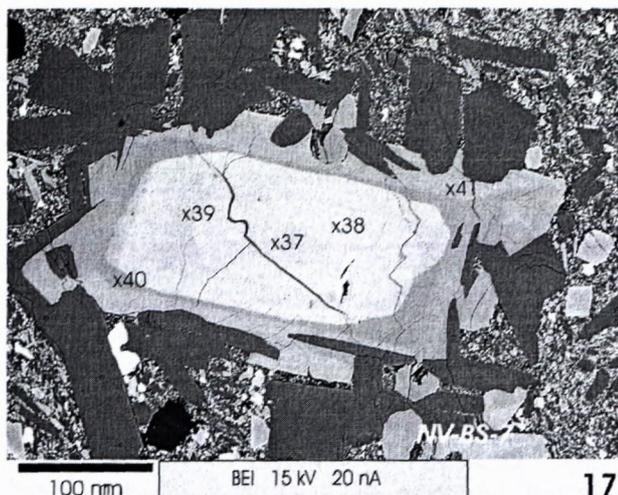
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Phototables: Zoned clinopyroxenes from alkaline basalt, Banská Štiavnica, Kalvária.  
Abbreviations: CC – carbonate, Pl – plagioclase

Standards used for elements: Si, Ca - wollastonite, Al -  $\text{Al}_2\text{O}_3$ , Ti -  $\text{TiO}_2$ , Fe - hematite, Mg -  $\text{MgO}$ , Mn - Mn, rhodonite, Na - albite, K - orthoclase, Cr - chromite.

Clinopyroxenes are recalculated to 6 oxygens and 4 cations.  $\text{Fe}^{3+}$  was calculated by charge balance. An analysis was recalculated to 4 cations exactly and  $\text{Fe}^{3+}$  was calculated as difference between 12 and total charge of cations.

#### Characteristics of zoned clinopyroxenes from Banská Štiavnica

The basanite from Banská Štiavnica - Kalvária comprises some types of zoned clinopyroxenes which differ in size, optical properties and chemical composition. Individual color hues of pyroxenes described below were observed in optical microscope at plane polarized light.

There are two basic types of the zonation in the studied rocks: continuous and discontinuous. *Continuously zoned* crystal comprises only one type of pyroxene which can have various hues of sandy and brown color. This type of zonation is typical for the most of pyrox-

enes. *Discontinuously zoned* crystal comprises two different types of pyroxenes which also differ in the color (some pyroxenes mentioned above which contain green cores).

Pyroxenes also have concentric, oscillatory, sector and non-regular (individual zones have non-regular shape) zoning.

In the clinopyroxene phenocrysts we can recognize three typical zones: (1) *central core or central part of phenocryst*, (2) *mantle* and (3) *rim*. The rim is narrow or is not present in some cases.

#### Pyroxenes with various hues of brown and sandy color

The most common types of pyroxenes in studied rocks are those of various hues of brown and sandy color in all parts of a crystal (photo 2, 3, 4). Color hue is determined by the concentration of Ti in an individual part of crystal. The higher is Ti content, the deeper is the color. Sandy color is more typical for the inner parts of clinopyroxenes, deep brown for their rims.

*Zoning* is a typical feature of these pyroxenes. There are some types of zonation: oscillatory, concentric, sector, non-regular. The optical zonation is of two kinds. *Simply zoned* crystal has inner part of sandy color and deep brown rim of various thickness. Deep brown clinopyroxenes in some samples can be added to this group. More color hues in a single phenocryst are typical for *more complicated zonation*, e. g. pyroxenes with brownish core, complex-zoned pyroxenes (photo 3, 4, 15).

The pyroxenes of this group are relatively often rounded and embayed. Inclusions of Ti-magnetite are concentrated to the rim parts of phenocrysts and to deeper brown pyroxenes.

### Green clinopyroxene cores

Some clinopyroxenes in the studied alkaline basalt contain green cores which are rimmed by mantle and rim of sandy and/or deep brown color. We can recognize two types of these green cores:

*Type I.* represent relatively wide group of pleochroic or weakly pleochroic cores with green - brown pleochroism. These two colors have various hues (photo 1, 5, 7, 11, 12, 13, 16, 17, 18, 20). These cores are mostly anhedral. They have variable optical intensity observed at plane polarized light. There are cores which are not very distinctive from mantling pyroxene to intense cores. The boundary between the core and the mantle can be sharp or more diffuse. They are unzoned or they have non-regular zoning at crossed polars. The shape of some cores resembles fragments. They are often rounded and embayed, what indicates resorption prior to the mantle overgrowth. These cores practically do not contain inclusions. If they do, these inclusions extend also to mantling pyroxene.

*Type II.* represents non-pleochroic, weakly pleochroic to pleochroic cores of light pale green color (photo 6, 9, 10, 14). These cores are mostly anhedral, rarely subhedral. They are mostly non-zoned at crossed polars. They contain tiny inclusions; in some cases inclusions rim this core what can suggest a resorption. Resorption can be reflected also by rounded and embayed shapes of cores.

Some *clinopyroxenes with composite core* were identified in studied samples - one core is rimmed by the another core, but there are cores of only one type in a single crystal (either the core of type I. - photo 17, or the core of type II. - photo 6). The composite cores are described also by Dobosi and Fodor (1992) in Novohrad region.

### Chemical composition of clinopyroxenes

Analyses of studied clinopyroxenes are listed in Tab. 1.

Clinopyroxenes were classified in quadrilateral En-Fs-Wo diagram (the I. M. A. classification, Morimoto et al., 1988, fig. 3). According this diagram almost all studied clinopyroxenes are *diopsides*. But it must be mentioned that these pyroxenes, besides cores of type II., contain

substantial amounts of non-quadrilateral components (mostly Al, less Na, Fe<sup>3+</sup>, Ti) and extensive substitution of these components probably raises values of Wo member (Bédard et al., 1988).

Higher contents of titanium (0,66 - 5,12 % TiO<sub>2</sub>) are typical for sandy and deep brown parts of clinopyroxenes. This type of pyroxene is described as *titanaugite* (e. g. Duda and Schmincke, 1985; Dobosi, 1989); in this work they will be named *Ti-augites* and *Ti-diopsides* (according classification). Parts of pyroxenes with more than ≈ 3,7 % TiO<sub>2</sub> can be according I.M.A. classification named as *titanian diopsides*.

One core with relatively high Mg number (Mg# = 0,86) and Cr<sub>2</sub>O<sub>3</sub> = 0,91 % can be termed *chromian augite*.

Green cores of type I. correspond on the basis of similar optical properties and chemical composition to *fassautes* and *fassaitic augites* (napr. Duda and Schmincke, 1985; Dobosi, 1989). Dobosi and Fodor (1992) named these clinopyroxenes *ferrous aluminous titaniferous diopsides*. They are characteristically enriched in Al (2,63 - 10,20 % Al<sub>2</sub>O<sub>3</sub>) and Fe<sup>3+</sup> so they can be according I.M.A. nomenclature named *ferrian aluminian augites and diopsides*.

Green cores of type II. were described as *salites* and *ferrosalites* (Dobosi, 1989). They probably correspond also to *acmitic augites* in the work of Duda and Schmincke (1985). According I.M.A. nomenclature we can name them *Fe-rich diopsides and augites* (c.f. Dobosi - Fodor, 1992).

We studied the compositional variability of zoned clinopyroxenes from the studied rock at variation diagrams. We compared contents of choosen elements in individual parts of pyroxene phenocrysts, i.e. in the core, mantle and rim. The trends of the compositional change in these parts of phenocrysts were also studied. The results were compared with the data from analogical phenocrysts in alkaline basalts from two regions: Novohrad (Dobosi, 1989; Dobosi and Fodor, 1992) and Eifel (Germany, Duda and Schmincke, 1985). Si, Al, Ti and Na contents and Mg/Fe ratios are the most variable.

Diagram **Si vs. Al** (fig. 4) shows two relatively linear trends. One is formed by the green cores, inner parts and mantles and the second by the rims of pyroxenes. Both of the trends have negative slope - decreasing Si contents at increasing Al contents.

This diagram also informs us about filling of Si deficiency in tetrahedral coordination by Al (Al<sup>IV</sup>). A deviation from line Si+Al=2 corresponds to the amount of Al in regular octahedral coordination (Al<sup>VI</sup>). The lower is Si content the higher is this amount. Rims and green cores of type II. have lower Al<sup>VI</sup> than another parts of clinopyroxenes.

Diagram **Mg/(Mg+Fe<sup>2+</sup><sub>sum</sub>; Mg#) vs. Fe<sup>3+</sup>** (Fig. 5) shows variability in Mg and Fe contents in the individual parts of pyroxene phenocrysts. Parts of pyroxenes of sandy and deep brown color are richer in Mg than green cores.

Iron was analyzed as Fe<sup>2+</sup>. Fe<sup>3+</sup> was calculated by charge balance. The green cores of type I. have the highest Fe<sup>3+</sup>. *Ti-augites* and *Ti-diopsides* have a trend of Fe<sup>3+</sup>

Table 1 of zoned clinopyroxenes from alkaline basalt, Banská Štitanica

	1 1	1 2	1 3	1 4	1 5	1 6	1 7	1 b 8	1 b 9	1 b 10	1 b 11	1 b 12	1 b 13	3 14	3 15	3 16
NV-BSS																
SiO <sub>2</sub>	47.94	46.08	47.36	44.17	49.54	45.08	43.97	51.44	51.22	42.98	44.03	44.69	48.65	52.33	45.43	43.34
TiO <sub>2</sub>	1.12	2.23	2.13	4.52	1.42	3.14	4.90	0.36	0.38	4.78	2.71	3.16	1.89	0.66	2.78	4.56
Al <sub>2</sub> O <sub>3</sub>	5.25	8.25	7.28	8.02	6.02	9.30	8.35	1.72	1.68	9.34	10.20	10.53	6.35	3.68	9.65	9.21
FeO	12.48	8.73	6.24	8.24	6.49	6.75	8.28	13.02	12.71	8.16	9.02	6.85	6.12	5.01	5.95	7.36
MnO	0.53	0.35	0.06	0.18	0.13	0.08	0.18	0.76	0.78	0.10	0.15	0.06	0.12	0.10	0.10	0.09
MgO	9.73	12.64	14.01	11.96	14.76	12.66	11.56	10.37	10.68	11.18	10.40	12.43	14.49	17.57	12.85	11.31
CaO	21.89	21.27	22.30	22.43	20.77	22.11	22.42	21.84	22.06	22.37	22.11	21.62	21.75	20.22	22.02	22.86
Na <sub>2</sub> O	0.98	0.69	0.57	0.57	0.61	0.59	0.70	0.92	0.88	0.67	0.88	0.70	0.51	0.55	0.72	0.71
K <sub>2</sub> O	0.00	0.00	0.00	0.01	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr <sub>2</sub> O <sub>3</sub>	0.01	0.00	0.35	0.00	0.09	0.08	0.00	0.00	0.00	0.00	0.03	0.02	0.21	0.30	0.25	0.06
Sum	99.93	100.24	100.30	100.10	99.83	99.79	100.38	100.43	100.39	99.58	99.53	100.06	100.09	100.42	99.75	99.50
Si	1.836	1.728	1.756	1.669	1.831	1.688	1.658	1.957	1.949	1.633	1.673	1.666	1.799	1.901	1.694	1.644
Al	0.237	0.365	0.318	0.357	0.262	0.410	0.371	0.077	0.075	0.419	0.457	0.463	0.277	0.158	0.424	0.412
Ti	0.032	0.063	0.059	0.128	0.039	0.089	0.139	0.010	0.011	0.137	0.077	0.089	0.053	0.018	0.078	0.130
Fe <sup>2+</sup> <sub>sum</sub>	0.400	0.274	0.194	0.261	0.201	0.211	0.261	0.414	0.405	0.259	0.287	0.214	0.189	0.152	0.186	0.234
Mn	0.017	0.011	0.002	0.006	0.004	0.003	0.006	0.025	0.025	0.003	0.005	0.002	0.004	0.003	0.003	0.003
Mg	0.556	0.707	0.775	0.674	0.813	0.706	0.650	0.588	0.606	0.634	0.589	0.691	0.799	0.951	0.714	0.640
Ca	0.898	0.855	0.886	0.908	0.822	0.887	0.906	0.890	0.899	0.911	0.900	0.864	0.862	0.787	0.880	0.929
Na	0.072	0.050	0.041	0.041	0.044	0.043	0.051	0.068	0.065	0.049	0.065	0.051	0.037	0.039	0.052	0.053
K	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.000	0.000	0.000	0.000	0.003	0.002	0.000	0.000	0.000	0.000	0.001	0.001	0.006	0.009	0.008	0.002
Sum cat.	4.048	4.053	4.041	4.044	4.019	4.039	4.043	4.029	4.035	4.045	4.054	4.041	4.026	4.018	4.039	4.047
Fe <sup>3+</sup>	0.145	0.154	0.123	0.133	0.058	0.115	0.129	0.085	0.104	0.133	0.159	0.117	0.076	0.052	0.114	0.136
Mg#	0.582	0.721	0.800	0.721	0.802	0.770	0.714	0.587	0.599	0.710	0.672	0.764	0.809	0.862	0.793	0.732
WO	48.436	46.569	47.763	49.267	44.771	49.169	49.862	47.040	47.068	50.499	50.676	48.841	46.595	41.640	49.438	51.525
EN	29.989	38.508	41.779	36.571	44.281	39.135	35.773	31.078	31.728	35.144	33.164	39.062	43.189	50.317	40.112	35.496
FS	21.575	14.924	10.458	14.162	10.948	11.696	14.364	21.882	21.204	14.357	16.160	12.097	10.216	8.042	10.449	12.978

NV-BS	3 17	3 18	3 19	3 20	3 21	3 22	3 23	4 24	4 25	4 26	4 27	4 28	4 29	4 30	4 31	4 32
SiO <sub>2</sub>	51.01	49.98	51.02	46.80	44.85	46.99	47.05	45.57	48.52	47.48	51.07	43.22	47.60	45.05	48.18	48.08
TiO <sub>2</sub>	0.17	1.29	0.16	3.71	2.58	2.26	3.43	2.23	1.83	2.17	0.26	3.91	2.09	2.90	1.81	2.50
Al <sub>2</sub> O <sub>3</sub>	1.07	2.63	1.10	6.45	9.74	7.63	5.79	9.66	6.85	7.77	1.49	10.34	7.34	9.36	6.60	5.22
FeO	17.00	11.69	17.24	7.22	8.76	6.08	7.10	8.21	5.72	6.28	13.54	6.99	6.30	7.95	6.06	5.22
MnO	1.11	0.54	1.29	0.11	0.18	0.10	0.15	0.22	0.10	0.12	0.82	0.15	0.14	0.13	0.12	0.14
MgO	9.25	11.78	9.28	13.02	11.38	13.43	13.04	11.28	14.25	13.76	11.04	11.60	13.54	12.17	12.17	13.54
CaO	19.99	21.90	19.65	22.65	21.52	22.10	22.81	21.85	21.75	21.82	20.21	22.20	21.93	20.98	21.94	22.58
Na <sub>2</sub> O	0.56	0.48	0.61	0.57	0.93	0.57	0.62	0.86	0.54	0.54	0.65	0.56	0.62	0.77	0.54	0.94
K <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.03	0.00	0.08	0.00	0.34	0.03	0.33	0.30	0.24	0.00	0.25	0.28	0.00	0.36	0.02
Sum	100.16	100.32	100.35	100.61	99.94	99.50	100.02	100.21	99.86	100.18	99.08	99.22	99.85	99.31	99.78	99.80
Si	1.974	1.894	1.972	1.744	1.690	1.754	1.764	1.708	1.795	1.758	1.965	1.636	1.770	1.699	1.790	1.800
Al	0.049	0.117	0.050	0.283	0.433	0.336	0.256	0.427	0.299	0.339	0.067	0.461	0.322	0.416	0.289	0.231
Ti	0.005	0.037	0.005	0.104	0.073	0.064	0.097	0.063	0.051	0.061	0.008	0.111	0.058	0.082	0.051	0.071
Fe <sup>2+</sup> <sub>sum</sub>	0.550	0.370	0.557	0.225	0.276	0.190	0.223	0.258	0.177	0.195	0.436	0.221	0.196	0.251	0.188	0.212
Mn	0.037	0.017	0.042	0.003	0.006	0.003	0.005	0.007	0.003	0.004	0.027	0.005	0.005	0.004	0.004	0.005
Mg	0.533	0.666	0.535	0.723	0.640	0.748	0.729	0.630	0.786	0.760	0.633	0.655	0.751	0.684	0.785	0.756
Ca	0.829	0.889	0.814	0.904	0.869	0.884	0.916	0.877	0.862	0.866	0.833	0.901	0.874	0.848	0.873	0.906
Na	0.042	0.035	0.046	0.041	0.068	0.041	0.045	0.062	0.039	0.039	0.048	0.041	0.045	0.056	0.039	0.069
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.000	0.001	0.000	0.002	0.000	0.010	0.001	0.010	0.009	0.007	0.000	0.008	0.008	0.000	0.011	0.001
Sum cat.	4.019	4.026	4.021	4.029	4.055	4.030	4.036	4.042	4.021	4.029	4.017	4.039	4.029	4.040	4.030	4.051
Fe <sup>3+</sup>	0.054	0.080	0.063	0.088	0.162	0.088	0.101	0.124	0.060	0.083	0.052	0.116	0.087	0.117	0.086	0.144
Mg#	0.492	0.643	0.490	0.763	0.699	0.797	0.766	0.709	0.816	0.796	0.592	0.748	0.793	0.732	0.807	0.781
WO	43.358	46.182	42.707	48.812	48.683	48.518	49.036	49.688	47.233	47.556	43.796	50.703	47.996	47.560	47.291	48.346
EN	27.877	34.597	28.069	39.039	35.854	41.054	39.026	35.694	43.068	41.735	33.281	36.860	41.241	38.362	42.524	40.342
FS	28.766	19.221	29.224	12.149	15.462	10.428	11.938	14.618	9.699	10.708	22.923	12.437	10.763	14.077	10.184	11.313

NV-BS	4 33	4 34	4 35	4 36	7 37	7 38	7 39	7 40	7 41	7 42	7 43	7 44	7 45	7 46	7 47	7 48
SiO <sub>2</sub>	44.76	46.54	49.14	42.83	48.87	46.05	48.45	45.75	41.15	44.54	51.67	48.06	49.11	46.84	44.21	42.59
TiO <sub>2</sub>	3.41	2.03	1.65	4.80	1.04	1.97	1.31	2.70	5.12	3.33	0.69	2.51	1.38	2.42	3.74	4.87
Al <sub>2</sub> O <sub>3</sub>	8.04	8.46	6.34	10.31	3.93	6.43	4.48	9.00	11.73	10.54	4.10	5.64	4.61	8.39	10.24	10.41
FeO	7.76	7.98	5.53	7.78	13.89	14.55	12.41	6.21	7.87	6.10	4.88	7.07	12.28	6.15	6.99	8.07
MnO	0.12	0.17	0.13	0.16	0.65	0.53	0.56	0.11	0.14	0.14	0.07	0.11	0.37	0.13	0.13	0.10
MgO	12.10	11.98	14.69	11.22	9.16	7.90	9.91	12.83	10.65	12.31	16.84	13.74	10.60	13.29	11.93	11.17
CaO	22.52	21.96	21.96	22.34	22.02	21.69	22.04	22.22	22.64	22.18	20.64	22.74	21.49	22.51	22.69	22.66
Na <sub>2</sub> O	0.69	0.84	0.46	0.70	0.93	1.14	1.03	0.54	0.56	0.72	0.58	0.44	0.90	0.57	0.50	0.56
K <sub>2</sub> O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.47	0.42	0.00	0.00	0.00	0.01	0.00	0.16	0.08	0.91	0.00	0.03	0.26	0.35	0.09
Sum	99.40	100.43	100.32	100.17	100.49	100.26	100.20	99.93	100.02	99.94	100.38	100.31	100.78	100.57	100.78	100.52
Si	1.697	1.738	1.808	1.615	1.873	1.781	1.851	1.706	1.560	1.661	1.883	1.790	1.856	1.733	1.647	1.604
Al	0.359	0.372	0.275	0.458	0.178	0.293	0.202	0.396	0.524	0.463	0.176	0.248	0.205	0.366	0.449	0.462
Ti	0.097	0.057	0.046	0.136	0.030	0.057	0.038	0.076	0.146	0.093	0.019	0.070	0.039	0.067	0.105	0.138
Fe <sup>3+</sup> <sub>sum</sub>	0.246	0.249	0.170	0.245	0.445	0.471	0.397	0.194	0.250	0.190	0.149	0.220	0.388	0.190	0.218	0.254
Mn	0.004	0.005	0.004	0.005	0.021	0.017	0.018	0.003	0.005	0.004	0.002	0.003	0.012	0.004	0.004	0.003
Mg	0.684	0.667	0.806	0.631	0.523	0.455	0.564	0.713	0.602	0.685	0.915	0.763	0.597	0.733	0.663	0.627
Ca	0.915	0.879	0.866	0.903	0.904	0.899	0.902	0.888	0.919	0.887	0.806	0.907	0.870	0.892	0.905	0.914
Na	0.051	0.061	0.033	0.051	0.070	0.086	0.076	0.039	0.041	0.052	0.041	0.032	0.066	0.041	0.036	0.041
K	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000
Cr	0.000	0.014	0.012	0.001	0.000	0.000	0.000	0.017	0.005	0.002	0.026	0.000	0.001	0.008	0.010	0.003
Sum. cat.	4.053	4.042	4.020	4.045	4.044	4.059	4.048	4.032	4.052	4.037	4.017	4.033	4.034	4.035	4.037	4.046
Fe <sup>3+</sup>	0.155	0.126	0.133	0.133	0.129	0.173	0.142	0.093	0.150	0.115	0.052	0.096	0.103	0.102	0.109	0.136
Mg#	0.735	0.728	0.720	0.720	0.540	0.491	0.587	0.786	0.707	0.783	0.860	0.776	0.606	0.794	0.753	0.712
WO	49.593	48.969	50.759	50.759	48.291	49.260	48.417	49.471	51.892	50.341	43.102	47.989	46.900	49.146	50.672	50.919
EN	37.073	37.159	35.469	35.469	27.938	24.932	30.274	39.721	33.992	38.876	48.930	40.370	32.183	40.386	37.122	34.930
FS	13.333	13.872	13.772	13.772	23.771	25.808	21.310	10.808	14.116	10.783	7.968	11.640	20.916	10.468	12.206	14.150

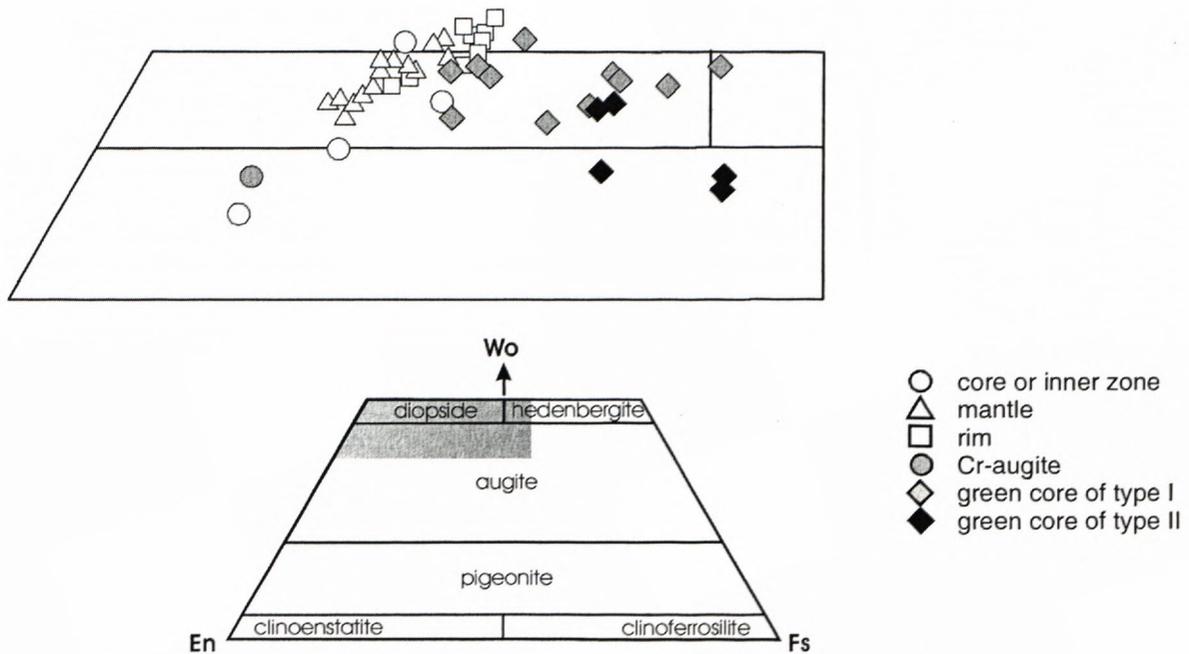


Fig. 3. Clinopyroxene classification. The part of clinopyroxene quadrilateral diagram shows the composition of various parts of clinopyroxenes from Banská Štiavnica.

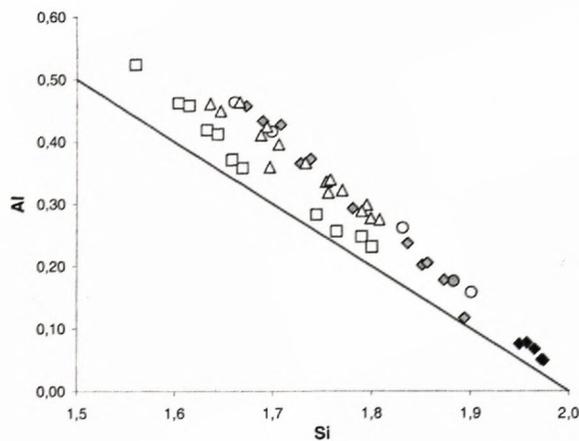


Fig. 4. Si vs. Al variation diagram. Symbols as for Fig. 3.

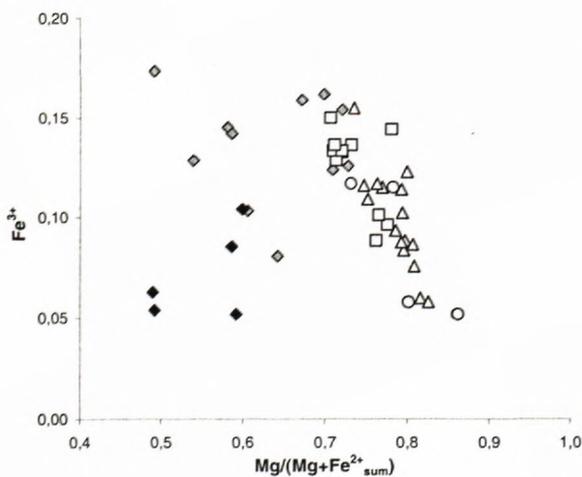


Fig. 5 Mg/(Mg+Fe<sup>2+</sup><sub>sum</sub>) vs. Fe<sup>3+</sup> variation diagram. Symbols as for Fig. 3

enrichment towards the rims which are typically enriched in Ti. Green cores of type II. have lower Fe<sup>3+</sup> contents than the cores of type I.. Fe<sup>3+</sup> can be bounded in the molecule of *esseneite* (Fe-Al-tschermakite)  $CaFe^{3+}AlSiO_6$ , respectively *aegirine*  $NaFe^{3+}Si_2O_6$ .

Relations between Al and Ti contents in the individual parts and types of clinopyroxenes are evident from diagram Al vs. Ti (fig. 6). Ti can be bounded in *Ti-tschermakite*  $CaTiAl_2O_6$  molecule. Ti:Al ratio in *Ti-tschermakite* has value 1:2. All studied types of clinopyroxenes have this ratio lower than 1:2 (predominance of Al). This fact suggests the presence of the another pyroxene molecules which can bound Al: *esseneite* mentioned above and/or mainly *Ca-tschermakite*  $CaAlAlSiO_6$ , respectively *jadeite*  $NaAlSi_2O_6$ .

Green cores of type II. have the highest Al/Ti ratio but the lowest Al and Ti contents of all studied pyroxenes. Al predominance over Ti is more expressive in the green cores of type I. and in the inner parts of phenocrysts (besides green cores) with Ti/Al ratio 1:4 to 1:8. The rims are richer in Ti (Ti/Al from 1:2 to 1:4).

Similar Al and Ti distribution, although more variable, can be seen in clinopyroxenes from Novohrad and Eifel (Duda and Schmincke, 1985; Dobosi, 1989).

Variation in Al<sup>IV</sup> and Al<sup>VI</sup> has connection with clinopyroxene genesis. Diagram Al<sup>IV</sup> vs. Al<sup>VI</sup> (Aoki and Kushiro, 1968; fig. 7) separated individual types of pyroxenes. Projection points of pyroxene rims are concentrated in the *field of igneous rocks*. Points of the other parts of phenocrysts are projected to the *field of granulites and inclusions in basalts* with corresponding higher Al<sup>VI</sup>/Al<sup>IV</sup> ratio. Green cores of type II. form individual group in this field (low Al<sup>IV</sup> a Al<sup>VI</sup>).

Diagram Mg/(Mg+Fe<sup>2+</sup><sub>sum</sub>) vs. Ti (fig. 8) demonstrates differences in the Ti contents in the dependance of Mg

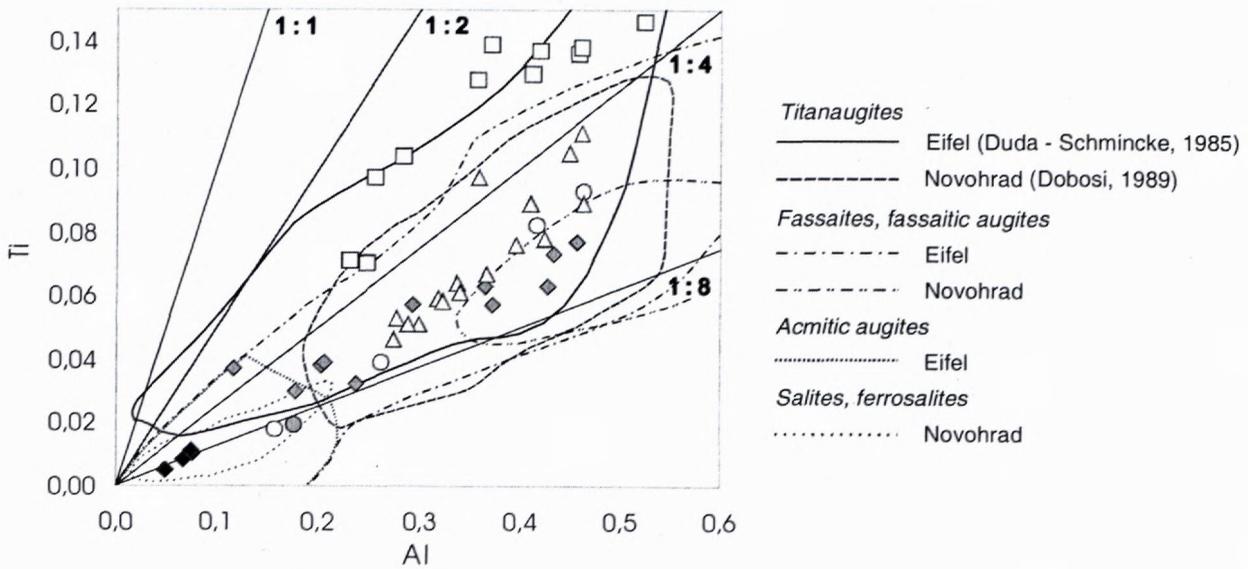


Fig. 6 Al vs. Ti variation diagram. Symbols as for Fig. 3.

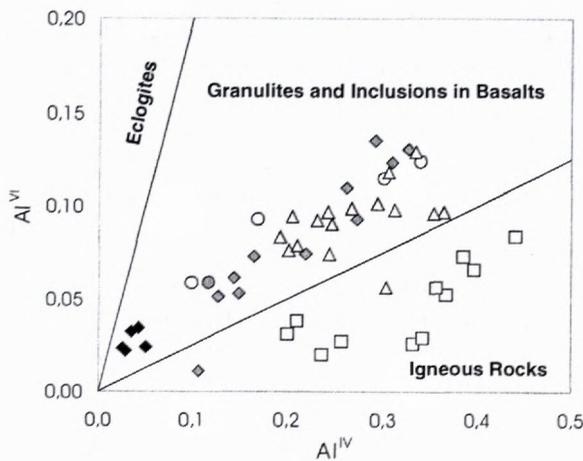


Fig. 7.  $Al^{IV}$  vs.  $Al^{VI}$  variation diagram. Symbols as for Fig. 3. Fields from Aoki and Kushiro (1968).

umber. Ti-augites and Ti-diopsides show relatively steep increase of Ti content with decrease of Mg number (increase of Fe at the expense of Mg). This phenomenon is typical for clinopyroxene fractionation from mafic alkaline melts (e. g. Tracy and Robinson, 1977). Analogical relations were observed also in the case of titanaugites from Novohrad and Eifel (Dobosi, 1989; Duda and Schmincke, 1985). The diagram also shows that Ti is concentrated predominantly to the rim parts of phenocrysts.

The green cores of type I. form in the diagram two separate groups. The first (close to the trend of Ti-augites and Ti-diopsides) has higher Mg number and Ti contents. It is placed in the field of fassaitic augites from Eifel (Duda and Schmincke, 1985) and titanaugites from Novohrad (Dobosi, 1989). The second group has lower Mg number and Ti contents and it is situated out of fields

formed by fassaites and fassaitic augites from Novohrad and Eifel. The green cores of type II. has low values for both of the components comparable with those of salites and ferrosalites in alkaline basalt from Novohrad region (Dobosi, 1989).

The Na contents demonstrated in  $Mg/(Mg+Fe^{2+}_{sum})$  vs. Na (fig. 9) diagram do not show considerable variations among individual parts of clinopyroxenes. But one can see higher Na contents of the green cores of type I. than Na contents of Ti-augites and Ti-diopsides. Na could be bounded in the molecule of aegirine  $NaFe^{3+}Si_2O_6$  and jadeite  $NaAlSi_2O_6$ .

## Discussion

The compositional variability of clinopyroxene phenocrysts in alkaline basalts is generally influenced by two factors: (1) the composition of a parental magma (material which individual types of clinopyroxenes have crystallized from and (2) P, T conditions of their crystallization.

### Ti-augites and Ti-diopsides

Mantles and cores of these composition are considered to have been formed in the magma (e.g. Duda and Schmincke, 1985). This is reflected by frequent zonality of this parts of the studied clinopyroxenes.

The interpretation of a cause of concentric or oscillatory zoning in a mantle of pyroxenes is still not clear. According Shimizu (1990) it is probably connected with alternation of periods of growing, stagnation and dilution, which can reflect changes in melt bulk composition, temperature, pressure and/or redox state.

The origin from magma can be suggested also for central parts of phenocrysts which have not pronounced shape of core.

Chemical composition of Ti-augites and Ti-diopsides gives us special information about conditions of their origin. The general trend shown in the direction pyroxene mantle - rim is Mg depletion, Ti enrichment and decrease in Al/Ti and  $Al^{VI}/Al^{IV}$  ratios (fig. 6, 7, 8). The decrease of Mg# towards pyroxene rims (e. g. fig. 8) can reflect a crystallization of the rim parts from more differentiated melt.

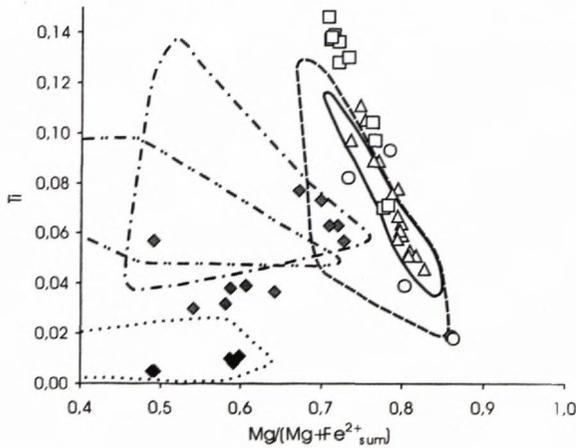


Fig. 8.  $Mg/(Mg + Fe^{2+}_{sum})$  vs. Ti variation diagram. Symbols and fields as for Figs. 3 and 6.

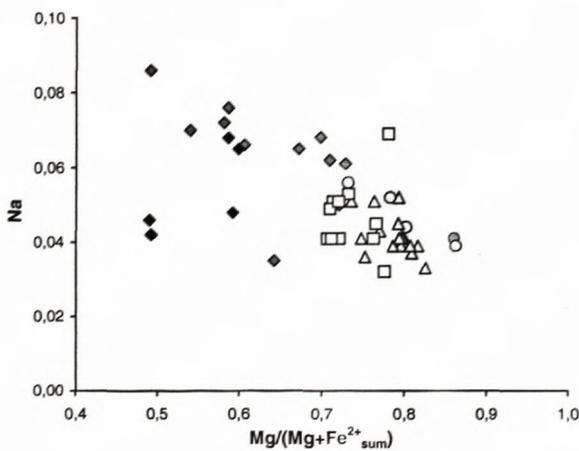


Fig. 9.  $Mg/(Mg + Fe^{2+}_{sum})$  vs. Na variation diagram. Symbols as for Fig. 3.

Changes in Ti composition cause color changes. The higher Ti content, usually the deeper brown color of pyroxene. It is considered that Ti contents are sensitive to pressure changes at pyroxene forming. Although the experimental data are to the some extent contradictory (Yagi and Onuma, 1967; Thompson, 1974; Edgar et al., 1980), one can assume that *Ti contents increase with decreasing pressure*. This can be confirmed by the fact that Ti is concentrated to the rim parts of clinopyroxene phenocrysts and groundmass clinopyroxenes, which formed later than inner parts of phenocrysts, at the higher levels of the crust or on the surface (c. f. Duda and Schmincke, 1985; Dobosi and Fodor, 1992; fig. 6 a 8).

Continuous trends in Ti and Fe contents in Ti-augites and Ti-diopsides (especially their mantles and rims) in presented diagrams demonstrate they had the same parental magma which had risen to the surface (c.f. Duda and Schmincke, 1985).

Al contents can similarly suggest the origin of the pyroxene rims at lower pressures than their inner parts. Diagram  $Al^{IV}$  vs.  $Al^{VI}$  (fig. 7) shows that the rims are projected in the field of low pressure magmatic clinopyroxenes (lower  $Al^{VI}/Al^{IV}$  ratio) while the inner parts are projected to the higher pressure field of granulites and inclusions in basalts.

The higher Ti/Al ratios of pyroxene rims (fig. 6) also indicate the origin at lower pressures (c.f. Dobosi and Fodor, 1992).

The calculations of Duda and Schmincke (1985) for titanite phenocryst mantle yielded temperatures of 1050 °C - 1140 °C and pressures 5-10 kbar. Thus, according these authors, this pyroxene zone appears to have crystallized at depths corresponding to the lower crust down to the crust/mantle boundary. Dobosi and Fodor (1992) have mentioned that clinopyroxene rims have formed at low pressure conditions, e. g. crystallization at shallow levels or at the surface after eruption.

A special problem is represented by the brown clinopyroxene cores present in some phenocrysts. Their composition (higher Ti content, lower Mg# and usually also higher Na) suggests crystallisation from more differentiated magma at probably higher pressure than the subsequent crystallisation of the mantling pyroxene. These cores can be connected with crystallization of gabbroic rocks in the uppermost mantle, respectively at the mantle/crust boundary. Xenoliths of this type with pyroxene of analogic composition were found in alkaline basalts (e. g. Colville and Novak, 1991; McGuire and Mukasa, 1997). The mantle of these brown cores which crystallized from less differentiated magma probably indicates entrapment of these cores by the injection of new, more primitive magma batch.

#### Cr-augite

Cr-augite core was found in the phenocryst in the sample NV-BS-7. It has anhedral shape and it is mantled by Ti-diopside. Wass (1979) and Duda and Schmincke (1985) interpreted cores of Cr-diopside composition as xenocrysts representing fragments of the upper mantle peridotite xenoliths. These xenocrysts served as nucleation sites for subsequent clinopyroxene crystallization (Dobosi, 1989). One can suggest that Cr-augites represent fragments of the upper mantle wall-rocks, which were trapped by rising basalt magma.

#### Green cores of phenocrysts

The green cores of studied phenocrysts are enriched in Fe and depleted in Mg if we compare them with mantling Ti-augites and Ti-diopsides. The cores of type I. have similar Al and Ti contents as inner parts of Ti-augite and

Ti-diopside composition, while the cores of type II. have the lowest concentrations of these elements from all of studied clinopyroxenes (fig. 6 and 8). The cores of type I. have the highest Na contents and the cores of type II. have the highest contents of Si (fig. 4 and 9).

There were some views at the origin of the green clinopyroxene cores in alkaline basalts:

1. *They are products of high-pressure differentiation trend of alkaline basalt magmas.*

Wilkinson (1975) mentioned that green clinopyroxene megacrysts represent very probably *the final fraction of clinopyroxene megacryst crystallization*. In this sense Wass (1979) presented that Fe-rich clinopyroxenes represent *an extension of the high-pressure Al-augite series clinopyroxene trend*.

2. *They are xenocrysts from more differentiated melt which was subsequently mixed with more primitive basic magma.*

The existence of mantle-derived differentiated melts has been well documented (e. g. Brooks and Printzlau, 1978; Irving and Price, 1981; Dobosi and Fodor, 1992; Bodinier et al., 1996) and also the possibility of mixing between more differentiated and mafic melt in the upper mantle environment (Bédard et al., 1988). But there is also the possibility that differentiated melt could originate by anatectic melting of crustal rocks (Philpotts, 1976) or metasomatized lower-crust rocks (Morogan and Martin, 1985).

Crystallization of Fe-rich clinopyroxenes and subsequent magma mixing could take place in the crust (Thompson, 1977; Barton et al., 1982) or in the upper mantle (Brooks and Printzlau, 1978; Wass et al., 1980).

According to Brooks and Printzlau (1978) green pyroxene cores have formed from *intermediate to salic magmas*. They suggest that more evolved melts, enriched in incompatible elements, probably originate by partial melting of metasomatically enriched mantle.

Duda and Schmincke (1985) suggest xenocrystic origin for fassaitic augites present in the cores of clinopyroxene phenocrysts. They are *xenocrysts which have formed from more differentiated magma*. This magma must have been enriched in Fe and incompatible elements, especially in phosphorus what is documented by inclusions of apatite in the cores. The cores formed in the depth of 15–30 km, possibly at the base of the crust.

Liotard et al. (1988) propose *high-pressure differentiated mugearitic magma with characteristically high REE contents* as a parental melt for acmite rich clinopyroxenes. This magma already had contained phenocrysts and subsequently was mixed with more primitive basaltic magma.

Dobosi and Fodor (1992) assume for the fassaitic cores the origin from *more differentiated magma(s) in the upper mantle magma chamber at high pressures*. This magma chamber was periodically filled with more primitive melts. Because of mixing of more differentiated melt which already had contained green cores with this more primitive magma, the green cores were mantled by the more mafic outer core or by the mantle. If the growing

clinopyroxene was trapped by more batches of more primitive magma, the multiple-zoned crystal has originated (e. g. inner core - outer core - mantle).

Pilet et al. (2002) note that green cores of clinopyroxenes have crystallized from *more evolved melts probably of phonolitic composition* at middle to high pressures in the upper mantle to the middle continental crust.

3. *They are xenocrysts from the upper mantle wall rocks.*

Brooks and Printzlau (1978) do not exclude the opportunity that some green cores could be *xenocrysts derived from the upper mantle wall rocks*. These xenocrysts were caught by basaltic magma which was rising through the upper mantle.

Barton and Bergen (1981) suggest the origin of green clinopyroxenes by *the upper mantle xenolith disaggregation*. These xenoliths reflect a local metasomatism or a crystallization from magmas of unknown composition during an earlier igneous event.

Dobosi and Fodor (1992) suggest that Fe-rich diopside cores come from *the upper mantle wall rocks and they are products of earlier event of partial melting and magma fractionation* than fassaitic augites.

Ivan and Hovorka (1993) presented the opinion that green salitic and/or ferrosalitic cores could have been *the products of the upper mantle peridotite metasomatic enrichment by rising melts and fluids*.

The next view of Ivan and Hovorka (1993) has a special place in this group of views. The fassaitic cores are probably products of metasomatism which is the result of the interaction between basaltic melts migrating through a vein system in the mantle and neighbouring mantle peridotite (Witt and Seck, 1989; McDonough and Frey, 1989; Bodinier, et al., 1990). These cores probably represent *disaggregated vein fillings*.

Shaw and Eyzaguirre (2000) describe clinopyroxene megacryst similar to acmites in the work of Duda and Schmincke (1985) which was found in the rocks from Eifel, Germany. This megacryst was probably derived from *the iron-rich cumulate in the upper mantle*.

*The green cores of type I.* can be assumed to be *xenocrysts*. It could be confirmed by the sharp optical and chemical boundary (higher Fe/Mg ratio) between the core and the mantle and the resorption (c. f. Duda and Schmincke, 1985).

These cores are mostly of anhedral shape. They are often rounded and embayed, what indicate the resorption prior the mantle growing (a dissolution of these cores in the melt). This resorption could have been due to an incorporation of these cores to hotter, pyroxene undersaturated mafic melt (Bédard et al., 1988).

The green cores of type I. from Banská Štiavnica basanite have not such optical intensity (intensity of the color) in many cases as have i. e. corresponding green cores from Novohrad region (fassaites and fassaitic augites, Dobosi, 1989). Brooks and Printzlau (1978) note that the intensity of green color is dependent at the content of acmite (aegirine) component  $\text{NaFe}^{3+}\text{Si}_2\text{O}_6$ . Really, although  $\text{Fe}^{3+}$  values are comparable for both the regions,

Na contents in the green cores of type I. (0,48 – 1,14 % Na<sub>2</sub>O) are lower than those in fassaites from Novohrad region (0,97 – 1,54 % Na<sub>2</sub>O).

We can observe relatively wide variability in the composition of the type I. cores at variation diagrams. This variability may be according Duda and Schmincke (1985) explained either as the influence of crystallization kinetics or, more likely, by every core crystallizing in a discrete magma batch of a certain degree of fractionation. Mg# of studied cores is lower than Mg# of pyroxene mantles of Ti-augite and Ti-diopside composition which rim these cores. This can suggest the *growing from the more differentiated melt* (cf. Duda and Schmincke, 1985; Dobosi and Fodor, 1992).

Especially at the diagram Mg# vs. Ti (fig. 8) we can see two groups of cores different in Mg, Fe and Ti contents: the first group with higher Mg# and Ti contents and the second one with lower Mg# and Ti contents. They do not create continuous Fe-differentiation trend as do fassaitic cores in pyroxenes from Novohrad (Dobosi and Fodor, 1992). It is possible that lack of more chemical analyses precludes to create a continuous trend but the existence of two types of more differentiated magmas cannot be also excluded. Especially the cores with subhedral shapes and the complex-zoned core with variable chemical composition could originate from more differentiated melt. The higher Al<sup>VI</sup>/Al<sup>IV</sup> ratios (field of granulites and inclusions in basalts, fig. 7), comparable with these ratios in clinopyroxene mantles suggest the crystallization at relatively high pressure.

Trace element investigation in megacrysts (Dobosi and Jenner, 1999) confirmed the origin of type I. green cores from alkaline basalt magma. Observed trace element relations and their correlation with changing Mg# can be explained by fractional crystallization of this magma in the upper mantle with the production of a range of fractionated melts. The results of xenolith study at various localities showed that these melts had crystallized in the uppermost mantle as veins of Al-pyroxene gabbro or pyroxenite (Richter and Carmichael, 1993), which can contain amphibole (Colville and Novak, 1991). Mechanism of the fractionation is not obvious, it is very probably the reaction of rising magma with wall rock mantle peridotites, which enriches magma in Al, Ca and Fe (Varfalvi et al., 1996).

It is possible to assume an alternative possibility of the origin of type I. cores (e. g. some cores have the shape which resembles fragments). Ivan and Hovorka (1993) note that these cores probably come from fillings of the vein system through which basalt magmas migrate in the upper mantle peridotite. The reaction of magma with carbonates cannot be also excluded. These carbonates in peridotites can originate as a result of the mantle metasomatism. Pyroxenes compositionally close to the green cores of type I. originate also at contacts of magma with dolomite carbonates (e. g. Shabynin et al., 1984; Bowman and Essene, 1984). Fragments of these green pyroxenes originate by desintegration of vein fillings by next batches of rising alkaline magma. They were consequently rim-

med by a mantle which have crystallized from basaltic magma.

*Green cores of type II.* are of two kinds. The first of them is represented by *anhedral, strongly resorbed cores*. On the basis of their optical characteristics and similar chemical composition (Fe, Mg, Al, Ti) with salite, ferrosalite and acmite cores (Duda and Schmincke, 1985; Dobosi, 1989), one can assume that they represent *fragments derived from the upper mantle wall rocks metasomatically enriched by rising melts and fluids* (e. g. Ivan and Hovorka, 1993). *The composite core* represent the second kind of core. It has an inner core with a fragmental shape at one of its edges. This inner core is mantled by zoned outer core of subhedral shape with partial resorption of edges. Compositionally it is not very different from the previous kind of cores although it is richer in Ti, Al and Na. It may originated in *more differentiated magma at higher pressures*. The origin from more differentiated magma can be suggested from core Mg# approximately 0,6. The origin at higher pressures is supported by Al<sup>VI</sup>/Al<sup>IV</sup> ratios comparable with green cores of type I. and higher Na contents (Fig. 7 and 9).

Unambiguous origin of green cores of this type is noted also by Duda and Schmincke (1985). They are not sure whether acmitic augites have originated in more evolved magma or they are the fragments of the upper mantle wall rocks. Space relations in the phenocrysts and strong resorption suggest they originated sooner than did fassaitic pyroxenes. Dobosi and Fodor (1992) suggest that these green cores present in the upper mantle wall rocks are products of earlier event of partial melting and magma fractionation than fassaitic augites.

Their low Mg# indicates the crystallization from strongly fractionated magma. But the REE pattern in a clinopyroxene megacryst similar to acmites from Eifel (Shaw and Eyzaguirre, 2000) is contradictory with the magma fractionation. This megacryst was probably derived from iron rich cumulate in the upper mantle.

There is also possibility of the continuous trend from cores of type I. to cores of type II.. This trend can be observed very well at the diagram Mg# vs. Ti (Fig. 8) and it could reflect strong differentiation of magma. There are the cores of both types (type I. and type II.) which may originate in magma. The question, whether such trend exists or both types of cores had different evolution, could be resolved by more analytical data, especially by trace element analyses.

## Conclusions

The results of this study of zoned clinopyroxenes in alkaline basalt from Banská Štiavnica, locality Kalvária can be summarized as:

- it can be assumed that their origin and evolution are similar to the genesis of analogical pyroxenes from the other areas (e. g. Novohrad and Eifel).

- Ti-augites and Ti-diopsides come from alkaline basalt magma, which does not reach high degree of differentiation. The variability in Ti and Al contents shows the

polybaric crystallization. The mantles with lower Ti content originated at higher pressures as did rim parts of phenocrysts with higher Ti contents.

– Cr-augites represent the fragments of the upper mantle wall rocks which were caught by rising basalt magma.

– The green cores of type I. originated in the melt or they represent disaggregated vein fillings in the upper mantle. Their magma origin can be assumed from zoning and subhedral shapes of some cores. The Mg# value and variability of chemical composition of these cores suggest more differentiated magmas of variable degree of differentiation. There is also possibility that the cores of type I. can represent disaggregated vein fillings (especially those with fragmental shape). Higher  $Al^{VI}/Al^{IV}$  ratios comparable with those of clinopyroxene mantles reflect the crystallization at relatively high pressure.

– Intensively resorbed cores of type II. are probably xenocrysts which originated in the upper mantle influenced by metasomatic processes. It is possible that some cores originated in differentiated magma (e. g. zoned subhedral core).

– There is a possibility of continuous trend from the cores of type I. to the cores of type II..

– Zoned clinopyroxenes in basanite from Banská Štiavnica - Kalvária are indicators of complex processes at alkaline magma evolution and its interaction with subcontinental mantle. They confirm inhomogeneity of this mantle, its probable veining and gradual evolution due to metasomatic processes, interaction of basaltic magma with wall rock peridotites and crystallization of part of basalt magma in the upper mantle or at the crustal-mantle boundary. All these processes took place prior to basalt magma rise to the surface.

## Acknowledgements.

## References

- Aoki, K. & Kushiro, I., 1968: Some clinopyroxenes from ultramafic inclusions in Dreiser Weiher, Eifel. *Contr. Mineral. Petrology*, 18, p. 326-337.
- Balogh, K., Miháliková, A. & Vass, D., 1981: Radiometric dating of basalts in Southern and Central Slovakia. *Západ. Karpaty, Sér. Geol.*, 7, p. 113-126.
- Barton, M. & Bergen, M. J., 1981: Green clinopyroxenes and associated phases in a potassium-rich lava from the Leucite Hills, Wyoming. *Contr. Mineral. Petrology*, 77, p. 101-114.
- Barton, M., Varenkamp, J. C. & Bergen, M. J., 1982: Complex zoning of clinopyroxenes in the lavas of Vulsini, Latium, Italy: evidence for magma mixing. *J. Volcanol. geotherm. Res.*, 14, p. 361-388.
- Bédard, J. H. J., Francis, D. M. & Ludden, J., 1988: Petrology and pyroxene chemistry of Monteregeian dykes: the origin of concentric zoning and green cores in clinopyroxenes from alkali basalts and lamprophyres. *Can. J. Earth. Sci.*, 25, p. 2041-2058.
- Bodinier, J. L., Vasseur, G., Vernieres, J., Dupuy, C. & Fabries, J., 1990: Mechanism of mantle metasomatism: Geochemical evidence from the Lherz orogenic peridotite. *J. Petrology*, 31, p. 597-628.
- Bodinier, J. L., Merlet, C., Bedini, R. M., Simien, F., Remaidi & M., Garrido, C. J., 1996: Distribution of niobium, tantalum, and other incompatible trace elements in the lithospheric mantle; the spinel paradox. *Geochim. cosmochim. Acta*, 60, p. 545-550.
- Bowman, J. R. & Essene, E. J., 1984: Contact skarn formation at Elkhorn, Montana I: p-T component activity conditions of early skarn formation. *Amer. J. Sci.*, 284, 597-650.
- Brooks, C. K. & Printzlau, I., 1978: Magma mixing in mafic alkaline volcanic rocks: the evidence from relict phenocryst phases and other inclusions. *J. Volcanol. geotherm. Res.*, 4, p. 315-331.
- Colville, A. A. & Novak, G. A., 1991: Kaersutite megacrysts and associated crystal inclusions from the Cima volcanic field, San Bernardino County, California. *Lithos*, 27, 107-114.
- Dobosi, G., 1989: Clinopyroxene zoning patterns in the young alkali basalts of Hungary and their petrogenetic significance. *Contr. Mineral. Petrology*, 101, p. 112-121.
- Dobosi, G. & Fodor, R. V., 1992: Magma fractionation, replenishment, and mixing as inferred from green-core clinopyroxenes in Pliocene basanite, southern Slovakia. *Lithos*, 28, p. 133-150.
- Dobosi, G. & Jenner, G. A., 1999: Petrologic implications of trace element variation in clinopyroxene megacrysts from the Nógrád volcanic province, north Hungary: a study by laser ablation microprobe inductively coupled plasma-mass spectrometry. *Lithos*, 46, p. 731-749.
- Duda, A. & Schmincke, H. U., 1985: Polybaric differentiation of alkali basaltic magmas: evidence from greencore clinopyroxenes (Eifel, FRG). *Contr. Mineral. Petrology*, 91, p. 340-353.
- Edgar, A. D., Condlife, E., Barnett, R. L. & Shirran, R. J., 1980: An experimental study of an olivine ugandite magma and mechanisms for the formation of its K-enriched derivatives. *J. Petrology*, 21, p. 475-497.
- Irving, A. J. & Price, R. C., 1981: Geochemistry and evolution of lherzolite-bearing phonolitic lavas from Nigeria, Australia, East Germany and New Zealand. *Geochim. cosmochim. Acta*, 45, p. 1309-1320.
- Ivan, P. & Hovorka, D., 1993: Geochemistry and petrology of the Late cenozoic alkali basalts of the Western Carpathians (Czechoslovakia). *Mineral. Petrology*, 48, p. 3-16.
- Konečný, V., Lexa, J., Halouzka, R., Hók, J., Vozár, J., Dublan, L., Nagy, A., Šimon, L., Havrila, M., Ivanička, J., Hojstričová, V., Miháliková, A., Vozárová, A., Konečný, P., Kováčiková, M., Filo, M., Marcin, D., Klukanová, A., Liščák, P. & Žáková, E., 1998: Geologická mapa Štiavnických vrchov a Pohronského Inovca. 1 : 50 000. Bratislava, Geologická služba Slovenskej republiky. I. diel 248 s., II. diel 473 s.
- Liotard, J. M., Briot, D. & Boivin, P., 1988: Petrological and geochemical relationships between pyroxene megacrysts and associated alkali-basalts from Massif Central (France). *Contr. Mineral. Petrology*, 98, p. 81-90.
- McDonough, W.F. & Frey, F.A., 1989: Rare earth elements in upper mantle rocks. In: Lippin, B. R. & McKay, G. A., eds.: *Geochemistry and mineralogy of rare earth elements*. Mineral. Soc. Amer., pp. 99-145.
- McGuire, A. V. & Mukasa, S. B., 1997: Magmatic modification of the uppermost mantle beneath the Basin and Range to Colorado Plateau Transition Zone; Evidence from xenoliths, Wikieup, Arizona. *Contr. Mineral. Petrology*, 128, 52-65.
- Miháliková, A. & Šímová, M., 1989: Geochemistry and petrology of the Miocene-Pleistocene alkali basalts of the middle and southern Slovakia. (In Slovak). *Západ. Karpaty, Sér. Mineral. Petrogr. Geoch. Lož.*, 12, p. 7-142.
- Morimoto, N. (1988): Nomenclature of pyroxenes. *Mineral. Petrology*, 39, p. 55-76.
- Morogan, V. & Martin, R. F., 1985: Mineralogy and partial melting of fenitized crustal xenoliths in the Oldoinyo Lengai carbonatitic volcano, Tanzania. *Amer. Mineralogist*, 70, p. 1114-1126.
- Pilet, S., Hernandez, J. & Villemant, B. (2002): Evidence for high silicic melt circulation and metasomatic events in the mantle beneath alkaline provinces: the Na-Fe-augitic green-core pyroxenes in the Tertiary alkali basalts of the Cantal massif (French Massif Central). *Mineral. Petrology*, 76, p. 39-62.
- Philpotts, A. R., 1976: Petrography of monts Saint-Bruno and Rougemont. *Ministère des Richesses naturelles du Québec, Publication ES-16*.
- Righter, K. & Carmichael, I. S. E., 1993: Mega-xenocrysts in alkali olivine basalts: Fragments disrupted mantle assemblages. *Amer. Mineralogist*, 78, p. 1230-1245.
- Shabynin, L. I., Pertzov, N. N. & Zotov, I. A., 1984: Problems of formation of ore-bearing skarns at the dolomite contacts (In Russian). Moscow, Nauka, 104 p.

- Shaw, C. S. J. & Eyzaguirre, J., 2000: Origin of megacrysts in the mafic alkaline lavas of the West Eifel volcanic field, Germany. *Lithos*, 50, p. 75-95.
- Shimizu, N., 1990: The oscillatory trace element zoning of augite phenocrysts. *Earth Sci. Rev.-s.*, 29, 27-38.
- Šímová, M. (1965): Petrography and petrochemistry of the final volcanism in the Slovenské stredohorie Mts. (In Slovak). *Acta geol. geogr. Univ. Comen.*, Geol., 9, p. 9-89.
- Thompson, R. N., 1974: Some High-pressure pyroxenes. *Mineral. Mag.*, 39, p. 768-787.
- Thompson, R. N., 1977: Primary basalts and magma genesis. III. Alban Hills, Roman comagmatic province, Central Italy. *Contr. Mineral. Petrology*, 60, p. 91-108.
- Tracy, R. L. & Robinson, N. P., 1977: Zoned titanium augite in alkali olivine basalt from Tahiti and the nature of titanium substitutions in augite. *Amer. Mineralogist*, 62, p. 634-645.
- Varfalvy, V., Hébert, R. & Bédard, J. H., 1996: Interaction between melt and upper mantle peridotites in the North Arm Mountain massif, Bay of Island ophiolite, Newfoundland, Canada: Implications for the genesis of boninitic and related magmas. *Chem. Geol.*, 129, p. 71-9.
- Wass, S. Y., 1979: Multiple origins of clinopyroxenes in alkali basaltic rocks. *Lithos*, 12, p. 115-132.
- Wass, S. Y., Henderson, P., Elliott, C. J., 1980: Chemical heterogeneity and metasomatism in the upper mantle: Evidence from rare earth and other elements in apatite-rich xenoliths in basaltic rocks from eastern Australia. *Phil. Trans. R. Soc. Lond. A*, 297, p. 222-246.
- Wilkinson, J. F. G., 1975: Ultramafic inclusions and high pressure megacrysts from a nephelinite sill, Nandewar Mountains, northeastern New South Wales, and their bearing on the origin of certain ultramafic inclusions in alkaline volcanic rocks. *Contr. Mineral. Petrology*, 51, p. 235-262.
- Witt, G. & Seck, H. A., 1989: Origin of amphibole in recrystallized and porphyroclastic mantle xenoliths from the Rhenish Massif - Implications for the nature of mantle metasomatism. *Earth Planet. Sci. Lett.*, 91, p. 327-340.
- Witt-Eickschen, G. & Kramm, U., 1998: Evidence for the multiple stage evolution of the subcontinental lithospheric mantle beneath the Eifel (Germany) from pyroxenite and composite pyroxenite/peridotite xenoliths. *Contr. Mineral. Petrology*, 131, p. 258-272.
- Witt-Eickschen, G., Seck, H. A. & Reys, Ch., 1993: Multiple enrichment processes and their relationships in the subcrustal lithosphere beneath the Eifel (Germany). *J. Petrology*, 34, p. 1-22.
- Yagi, K. & Onuma, K., 1967: The join  $\text{CaMgSi}_2\text{O}_6\text{-CaTiAl}_2\text{SiO}_6$  and its bearing on the titanaugites. *J. Fac. Sci. Hokkaido Univ., Series IV*, 13, p. 117-138.