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Cr-spinels from the Mesozoic alkali volcanic rocks of the Western Carpathians; mineralogy and petrology

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Introduction

Among heavy minerals found in Mesozoic volcanic rocks, spinel is of particular significance because unlike silicates it is resistant to mechanical breakdown and low – grade alteration; it is widespread accessory mineral in the Mesozoic alkali volcanics; spinel derived from mantle peridotites and volcanic rocks is indicative of magmatic and tectonic evolution; spinel chemistry is diagnostic for melt composition and crystallization condition. We have analyzed spinel from the Mesozoic alkali volcanics of the Central Western Carpathians.

Geology and petrology

Mesozoic (Cretaceous) alkali rocks of various types occur in the External and Central Western Carpathians. In the Central Western Carpathians, Mesozoic alkaline volcanism is known from the Tatric (envelope) units, the Krížna and Choč nappes. Besides these, penetrations of basanite dikes into granitoid rocks have been also reported. On the basis of stratigraphic data the age of volcanics under consideration is Barremian – Aptian, which is proved also by geochronological data (102 Ma, Spišiak and Balogh 2002). The products of the volcanic activity are low-differentiated rocks of basalt/basanite type, very rarely picrites; volcanoclastic rocks are represented in substantial amounts (hyaloclastites etc.). The majority of Mesozoic alkaline rocks (with the exception of picrites) are characterised by the presence of a fine-grained devitrified matrix (up to 40 %). Olivines, pyroxenes and to a lesser degree amphiboles form phenocrysts and locally they accumulate into glomerophyres. Olivines are totally replaced by chlorite-serpentine-carbonate aggregates. Clinopyroxenes are the determin-

ing and dominant minerals in all rock types. Besides phenocrysts of various shape and size, they form also microlites in the devitrified matrix. A characteristic feature of the clinopyroxenes is sector and oscillation zoning. According to the IMA pyroxene classification (Morimoto 1989), they correspond to diopside. Amphiboles are zonal and correspond to kaersutite or low-silicium kaersutite. From other minerals, there are rarely present feldspars, apatite, analcime, pseudoleucite, **spinels**, ore minerals, phlogopite and others (Spišiak and Hovorka 1997).

The geochemical patterns of Central Western Carpathians Mesozoic volcanics are very close to those of Mesozoic alkaline rocks from different parts of Europe (Moravian alkali rocks; Dostal and Owen 1998, North-Pyrenean rift zone; Azambre et al. 1992, Northern Calcareous Alps; Trommsdorff et al. 1990, etc.) and/or Cenozoic alkali basalts in Europe (Wedepohl. et al. 1994,Wilson and Downes1991). Based on alkali character of volcanics under consideration we suppose that Cretaceous volcanism of the Central as well as External Western Carpathians was in close connection to rifting processes. Such processes lasted for a short-time and in the following time-period compressional processes took part, which blocked communication paths of magma (Hovorka and Spišiak 1988, Hovorka et al. 1999).

Mineralogy

The size of spinel grains (octahedral crystals and fragments) is in average about 300-500 μm. Spinels from Mesozoic volcanics show significant variation in chemistry. We have distinguished few principal compositional groups according to spinel chemical composition:

1. upper-mantle peridotitic spinel (Podmanín, Dobrá, Slopná)

2. volcanic spinel:

a.) Cr-spinel (Podmanín, Dobrá, Slopná, Košeca, Čebraď)

b.) Fe-Ti spinel (Podmanín, Dobrá, Štepnica, Osobitá)

3. altered spinel (all of studied localities)

Peridotitic and volcanic spinel can be easily discriminated on the basis of their TiO_2 content and Fe^{2+}/Fe^{3+} ratio. Volcanic spinels tend to have content of TiO_2 $> 0{,}2$ wt % and ratio $Fe^{2+}/Fe^{3+} < 4$ (Kamenetsky et al., 2001).

Peridotitic spinel occurs in Podmanín, Slopná and Dobrá locality. Sample from Podmanín has the highest content of Al_2O_3 (about 60 wt %) among the all studied samples. Content of TiO_2 is very low (up to 0,10 wt %). Mg# ($Mg/Mg+Fe^{2+}$) values ranges from 79-81 mol % and Cr# (Cr/Cr+Al) ranges between 7-12 mol %. The low-

est content of Al_2O_3 (36-48 wt %) has sample from Dobrá. Peridotitic spinel from this localities should come from mantle peridotites, otherwise into volcanic rocks could be integrate during up-lift of alkali volcanic rock.

Among volcanic spinel type has very similar composition sample from Podmanín and Čebrad'. Content of Al_2O_3 ranges from 34-39 wt % and content of TiO_2 ranges between 0,88-1,09 wt %. Mg# values ranges between 71-74 mol % and Cr# values ranges from 28-35 mol %. These composition correspond to spinel from volcanites. Volcanic spinels from Podmanín and Čebrad have in addition to chemistry also other similar features: a/ usually are concentrically-zoned, b/ often contain silicate/melt inclusions. Concentric zonation is caused by different content of trivalent cations Al^{3+} and Cr^{3+} that is about 4 wt% of Al_2O_3 alternatively Cr_2O_3 in individual zones.

Fe-Ti spinels have been found in Podmanín, Dobra, Štepnica and Osobitá. There are only spinel varietes on some localities (Štepnica, Osobitá). These spinels are associated with clinopyroxene Cpx) and apatite in Dobrá and Štepnica locality. Fe-Ti spinels from these localities has identical chemical composition as well. The amount of ulvöspinel (usp) component is between 8-38 mol %. The distinctive feature of spinels from alkalic rocks is their tendency toward high Al_2O_3content, particularly in basanites (Frost and Lindsley, 1991). Al_2O_3 content is in average 3 wt %. Textural feauteres and chemical composition of some titanomagnetites suggest the low temperature ($<$300-400°C) oxidation, especially in the presence of hydrothermal solutions, cation-deficient spinels (titanomaghemites) are formed in which some vacancies appear in the iron cation sites (Banerjee, 1991). The most important occurrence of titanomagnetites is in the center of the median valley of MOR while titanomaghemites occur in the altered pillow basalts.

Alteration processes are apparently recognized on all of the studied localities. In addition to chemistry changes, textural changes was observed as well. By alteration processes are affected mainly volcanic spinels. The strongest changes in spinel chemistry was observed in Košeca, where are altered almost all of the spinel grains. Alteration is affecting spinel grains from their margins by production of rims enriched in TiO_2, Fe_2O_3 or Cr_2O_3. Progress of alteration is faster if spinel has weaker zones or fractures within the grains. There is recognized one trend of alteration: dissolution of Mg^{2+}, Al^{3+} and Fe^{2+}, Fe^{3+} and Ti-enrichment. Changes in Mn^{2+}, Zn^{2+} and V^{5+} are not so apparent. Altered spinels have slightly higher content of these elements.

Silicate and melt inclusions within the Cr-spinel

Silicate and melt inclusions trapped in spinel were found in volcanic spinel from Čebrad' and Podmanín. Shape of the inclusions is dominantly oval and their size is up to 40 μm, but in average about 20 μm. Some concentrically-zoned grains bound the

inclusions within the one zone. Inclusions which are affected by cracks are altered and filled with secondary minerals. Most of the inclusions contain two phases: clinopyroxene (Cpx) + plagiolase (Plg, locality Čebrad') or Cpx + melt (Podmanín). Single phase inclusions contain Cpx or melt.

Clinopyroxene

Cpx has the composition $Wo_{30,31-49,43}En_{37,58-54,36}Fs_{9,36-16,94}$and according to Morimoto (1989) nomenclature, these samples correspond to augite and diopside. These Cpx have higher TiO_2 (3,08-4,26 wt %) and Al_2O_3 (7,50-11,61 wt %) in comparison with Cpx from Štepnica, Dobrá and Podmanín. Content of Na_2O is in average about 0,70 wt %. Higher contents of Cr_2O_3 in some analyzes are caused by host-spinel contamination. Mg# (100Mg/Mg+$\sum$Fe) value ranges between 72,67-77,78 mol% (Čebrad') and between 80-82,28 mol % (Podmanín). These composition correspond to Cpx from alkali volcanic rocks.

Plagioclase and melt

Albite end-member is dominant in plagioclase inclusion from Čebrad'. Two phase inclusions are typical for Podmanin locality. These inclusions contain a shrinkage bubble. Composition of coexisting melt with Cpx is as follows: SiO_2 (44,67-46,98 wt %), TiO_2 (2,61-3,60 wt %), Al_2O_3 (15,90-17,99 wt %), FeO (6,54-8,70 wt %), MgO (3,33-9,04 wt %), CaO (6,13-7,72 wt %), Na_2O (3,02-4,47 wt %) and K_2O (1,07-3,05 wt %). These melt composition suggest alkali character of parental magma.

Conclusion

- We have distinguished few principal compositional groups according to spinel chemical composition: **1.** upper-mantle peridotitic spinels , **2**. volcanic spinels: a/ Cr-spinels , b/ Fe-Ti spinels, **3**. altered spinel
- Peridotitic spinel has the hihgest content of Al_2O_3 (about 60 wt %) and low content of TiO_2 (up to 0,10 wt %). Mg# (Mg/Mg+Fe^{2+}) values ranges from 79-81 mol % and Cr# (Cr/Cr+Al) ranges between 7-12 mol %.
- Volcanic spinel has Al_2O_3 content (34-39 wt %) and TiO_2 content (0,88-2,19 wt %). Mg# values ranges between 71-74 mol % and Cr# values ranges from 28-35 mol %. These composition correspond to spinel from volcanites.
- Compopsition of Fe-Ti spinels documented alkali character of parental magma as well.
- Silicate and melt inclusions were found in volcanic spinels. Inclusions which are affected by cracks are altered and filled with secondary minerals. Most of the

inclusions comprises two phases: clinopyroxene(cpx)+plagiolase (Plg, locality Čebrad') or Cpx+melt (Podmanin). Single phase inclusions contain Cpx or melt.

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