

# Subsolidus alkali metasomatism in the metamorphosed Ordovician acid volcanics and volcanoclastics of the Gelnica Group (Gemic Superunit, Western Carpathians)

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## AGEOS      Subsolidová alkalická metasomatóza metamorfovaných ordovických kyslých vulkanitov a vulkanoklastík gelnickej skupiny (Gemerikum, Západné Karpaty)

**Abstract:** The Early Paleozoic Gelnica Group (Gemic Superunit, Western Carpathians) is composed of low-grade metamorphosed flysch-like sedimentary complexes alternated with volcanogenic complexes built up mostly by acid volcanoclastic rocks. Volcanoclastic rocks and small rhyolite bodies Ordovician in age underwent subsolidus alkali metasomatism locally overprinted by multiple stages of younger metamorphic and hydrothermal alterations. The observed variability in chemical compositions indicates that the most of acid volcanic and volcanoclastic rocks experienced potassic or sodium metasomatic alteration, the unaltered or Mg-metasomatised rocks occur less frequently. The dominating K-metasomatism is related mainly to the K-feldspar, partly also biotite and muscovite/sericite formation at the expense of matrix or original feldspar phenocrysts. The Na-metasomatism is connected with albite formation. The highest concentrations of alkalies (up to 13.52 wt. % K<sub>2</sub>O and 7.08 wt. % Na<sub>2</sub>O respectively) have been found in rocks originally represented by glassy dacites. The elements like Al, Ti and Zr remain immobile in alkaline metasomatic processes in contrast to Rb or metals. Based on the results from areas with analogical geological structure and evolution, especially the Bergslagen area in Sweden, we suppose that alkali metasomatism in the Gelnica Group is a product of hydrothermal system caused by the infiltration and circulation of sea water. The areas with K-, Na- or Mg-metasomatism represent different parts of the original hydrothermal system, where the K-metasomatism was probably its lower temperature section. This hydrothermal system probably mobilised some metals (Cu, Pb, Zn, Fe, Mn) for the formation of stratiform sulfide and oxide mineralizations or served as the metal pre-concentrator for younger siderite-sulfide vein deposits.

**Keywords:** Western Carpathians, Gelnica Group, Early Paleozoic, acid metavolcanites and metavolcanoclastics, alkali metasomatism

## 1. INTRODUCTION

The hydrothermal metasomatic alteration is a typical feature of many huge acid volcanites and volcanoclastic complexes in the world. It leads to significant increase of the whole-rock K<sub>2</sub>O or Na<sub>2</sub>O content (alkali metasomatism), less often MgO content (Mg-metasomatism) and it is accompanied by the mobility of metals (Fe, Mn, Pb, Zn, Cu), what can result in the ore deposits formation (e. g. Lagerblad & Gorbatshev, 1985; Stephens et al., 2009). Study of this alteration has therefore great metallogenic and prospecting significance.

The Early Paleozoic Gelnica Group, built up mostly by low-grade metamorphosed acid volcanics and volcanoclastics belong to the most important metallogenic areas of the Western Carpathians. Although the hydrothermal metasomatic alteration of acid volcanic rocks from the Gelnica Group was identified many years ago (Gubač, 1977; Dianiška, 1983; Ivan & Stettner, 1987) and partly studied by several authors (Dianiška et al., 1985; Eliášová, 1988), these data are mostly disseminated in

unpublished manuscripts and more complex study is still missing. The aim of this paper is therefore to characterize processes related to the alkali metasomatism of acid volcanic rocks in the Gelnica Group by application of appropriate geochemical methods and using all present-day accessible geochemical data.

## 2. GEOLOGY

The Early Paleozoic (Cambrian-Devonian) volcano-sedimentary Gelnica Group is spatially the most extensive lithostratigraphic unit of the Gemic Superunit (Fig. 1). It is built up by volcanogenic rock complexes composed mainly of acid metavolcanoclastics as well as by complexes of metamorphosed psammitic and pelitic sediments inclusive subordinated black shales and locally also metamorphosed black cherts (lydites) or limestones (Ivanička et al., 1989). The effusive acid and mafic rocks (metarhyolites/metadacites and metabasalts) are present in small amounts only (Bajaník et al., 1983, 1984). In

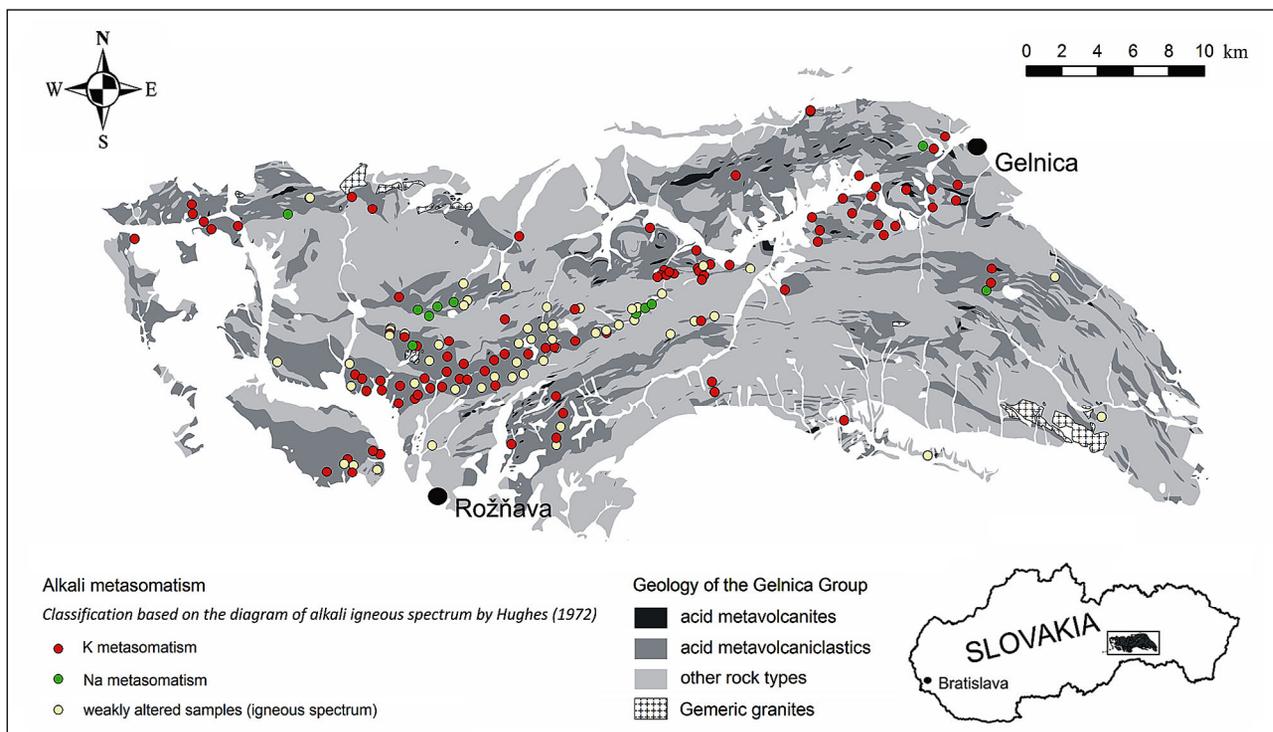


Fig. 1. Simplified geological map of the Early Paleozoic Gelnica Group (Gemic Superunit of the Western Carpathians) illustrating extent of acid volcanic and volcanoclastic rocks and localizing the most of studied samples which experienced potassic or sodic metasomatic alteration. Identification of type of the metasomatic alteration is based on the position of samples in the diagram on Fig. 4.

the volcanogenic complexes the low-grade metamorphosed rhyolite tuffs of various granularities are intercalated by phyllites originally representing fine-grained acid volcanoclastic material (Kamenický, 1954; Chmelík & Snopko, 1961; Ivan & Méres, 2005). Acid metavolcaniclastics of psammitic facies traditionally referred to as porphyroids dominate. Acid metavolcanics show arc geochemical signature (Vozárová & Ivanička, 1996; Ivan & Méres, 2005) whereas metabasalts beside calc-alkaline (CAB) type belong also to continental tholeiite (CT) and back-arc basin basalt (BABB) types (Ivan, 1993, 2009). Sedimentary clastic material of volcanogenic origin seems to dominate also in the complexes of sedimentary origin beside possible older continental source (Vozárová & Ivanička, 1993). Metamorphosed greywackes and quartzites are the most widespread petrographic rock types. A minor part of the autochthonous sediments is represented by silicites, limestones and black shales which contain significant admixture of organogenic material. The sedimentation style resembles the flysch complexes, what indicates the redeposition of material by turbidite currents (Ivanička et al. 1989). Only thin intercalations of acid volcanoclastics are embedded immediately among metamorphosed sediments.

The subdivision of Gelnica Group into smaller lithostratigraphic units (formations) has encountered several problems, neither one of the two existing concepts (Ivanička et al., 1989 vs. Grecula, 1982; Grecula et al., 2011) is completely in accordance with current knowledge (e.g. Ivan, 2009). The Gelnica Group is sporadically intruded by small bodies of the Permian granites (Uher & Broska, 1996). It forms an integral part of the

Alpine nappe structure of Gemic Superunit and it is probably built of several partial nappe units, however, their delimitation is still controversial (Grecula, 1982; Ivan, 1996).

The age of rocks included into the Gelnica Group is supposed to be from the Upper Cambrian to Lower Devonian (Snopková & Snopko, 1979; Ivanička et al., 1989; Vozárová et al., 1998; Vozárová et al., 2012). Acid volcanic rocks are Ordovician in age and were probably produced in two phases at ca. 490 and 465 Ma (Vozárová et al., 2010).

It is generally accepted that the Gelnica Group underwent regional metamorphism which did not exceed the lower greenschist facies conditions (ca. 350–450°C and 3–5 kbar – e.g. Sassi & Vozárová, 1987; Faryad, 1991<sup>a</sup>; Vozárová et al., 1998). Original concept of one-stage Variscan metamorphic alteration has been newly changed by the concept of multi-stage alteration including Variscan and Alpine stages of regional and local hydrothermal alteration, tectonometamorphism or thermal metamorphism at the contacts of granitic bodies (Vozárová et al., 2014). Alkaline hydrothermal-metasomatic alteration presented in this paper represents also one further stage in the complex metamorphic evolution of the Gelnica Group.

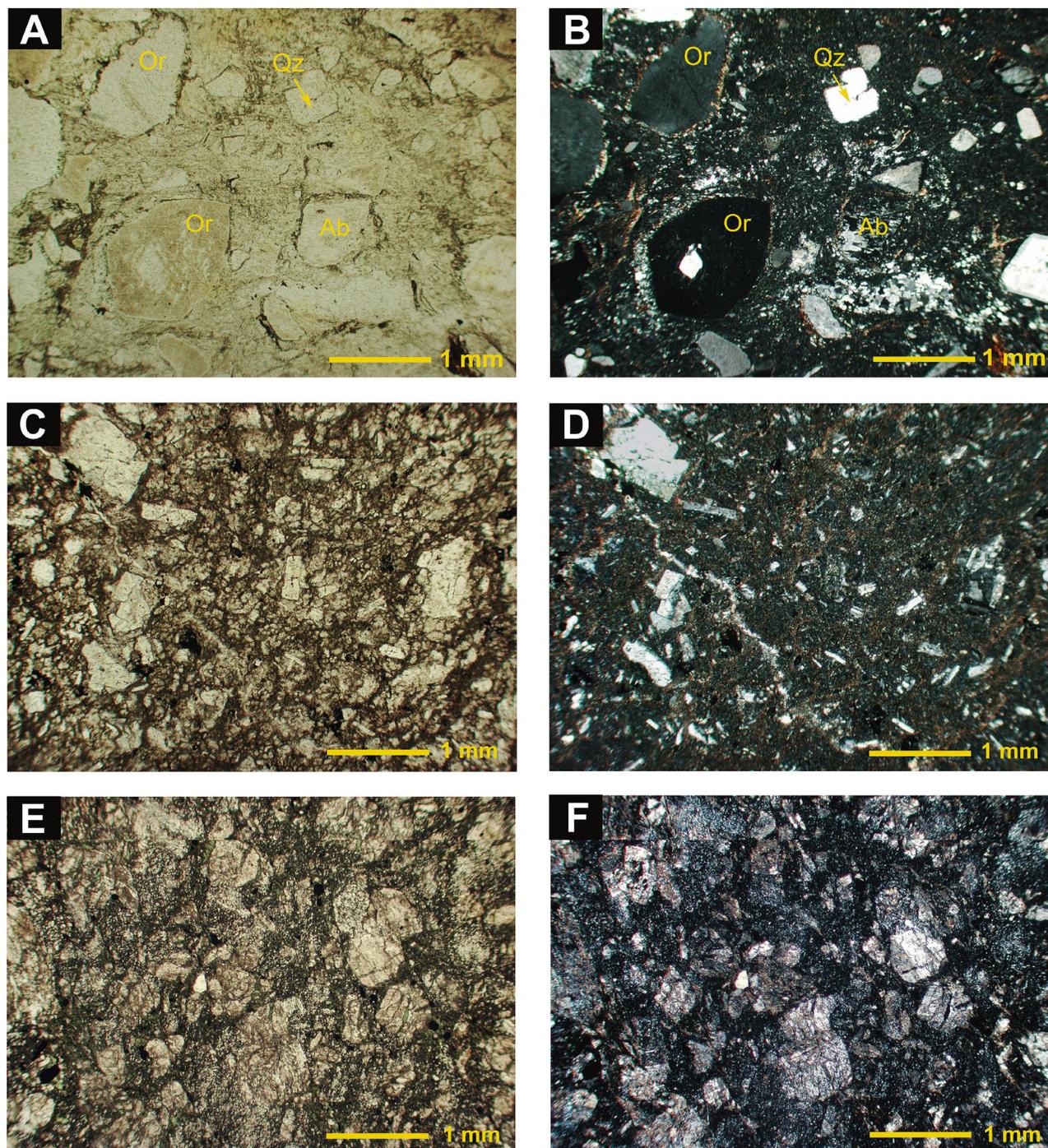
There are many analogues of the Gelnica Group (including the topic under study) in the Eastern Alps, Southern Alps, in Sardinia, Sicily as well as in the Eastern Carpathians. Despite older age (Proterozoic), the Bergslagen area in Sweden (e.g. Stephens et al., 2009) is also similar to Gelnica Group in many parameters (lithology, alkali metasomatism or metallogeny).

### 3. PETROGRAPHY OF THE ACID METAVOLCANIC ROCKS

Acid metavolcaniclastics are the most widespread rock types of the Gelnica Group (about 40%). The effusive varieties are represented

in less than 1%. Besides the effusive varieties (metarhyolites, metadacites) this work deals only with the acid metavolcaniclastics of psammitic fraction, traditionally called „porphyroids“.

The characteristic feature of metamorphic acid volcanites and volcaniclastics of the Gelnica Group is their variability in



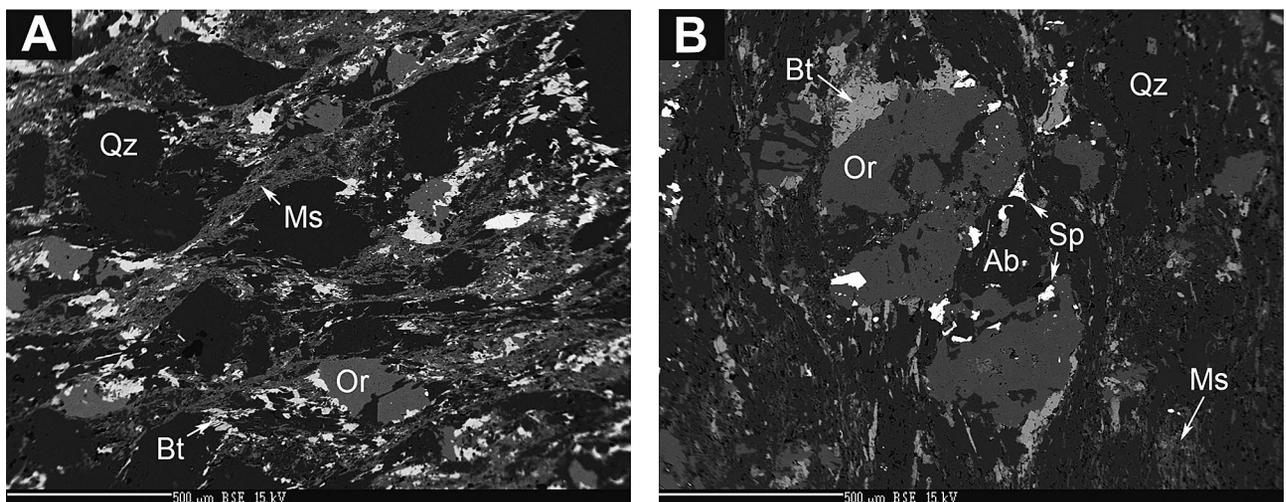
**Fig. 2.** Microphotographs of the acid volcanic rocks from Gelnica Group affected by intensive alkaline hydrothermal-metasomatic alteration. **A:** Rhyolite altered by K-metasomatism (9.12 wt. %  $K_2O$ ) with phenocrysts of quartz (Qz) and orthoclase (Or), a part of feldspar phenocrysts is replaced by chess-board albite (Ab), small flakes of metamorphic biotite are concentrated into small veins and aggregates (parallel nicols, sample BSL-37, quarry at the N border of Helcmanovce village). **B:** the same, crossed nicols. **C:** primary glassy dacite with some orthoclase phenocrysts altered by K-metasomatism (13.52 wt. %  $K_2O$ ; parallel nicols, sample BSL-85, Lacemberg Valley ca. 1 km W from Holica hill, 859 m asl). **D:** the same (crossed nicols). **E:** porphyritic dacite altered by Na-metasomatism (6.74 wt. %  $Na_2O$ , 1.18 wt. %  $K_2O$ ) with phenocrysts replaced by albite, with sericite and chlorite mostly in groundmass and also with small grains Fe-Ti oxides (parallel nicols, sample FD-154, ca. 1 km N from the Dobšinská Píla settlement, eastern slope of the Peckenberg hill, 634.2 m asl).

colour and texture resulting from the combination of primary petrographic differences and more types of alterations. The metarhyolites are massive rocks of brown-grey, brown, white, grey and greenish colour, which contain macroscopically visible phenocrysts of quartz, feldspar and completely altered biotite. Microscopically, the metarhyolites are characterized by porphyric texture with the microgranoblastic or microlepidogranoblastic texture of matrix (Fig. 2A-B). The ratio of phenocrysts to groundmass is variable, also originally glassy types with small amounts of phenocrysts have been found. Phenocrysts are represented by quartz, K-feldspar and albite, the last one mostly as chess-board variety. Magmatic corrosion is typical mainly for quartz phenocrysts. The original magmatic biotite is pseudomorphed by aggregates of secondary metamorphic biotites and/or by chlorite, muscovite and ore pigment. Rare amphibole phenocrysts replaced by chlorite, epidote, calcite and titanite have been also found. The groundmass of metarhyolites comprises a fine-grained aggregate of quartz and feldspar with less amount of sericite, metamorphic biotite or chlorite. The content of carbonate and quartz which are formed at the expense of chlorite and feldspar increases in the vicinity of the siderite-sulfide veins. Zircon and Fe-Ti oxides are most common accessory minerals.

Rocks with the oriented structure and porphyric texture, which contain macroscopically visible phenocrysts of quartz and/or feldspar and possibly mafic minerals, are traditionally called as “*porphyroids*”. They include not only the acid metavolcaniclastics but also oriented effusive varieties. Macroscopically they form a wide range of varieties distinct in (1) colour (brownish black, dark grey, light gray, dark green, light green, brownish and yellow), (2) size and nature of phenocrysts and (3) mineral composition of the matrix. Microscopically the porphyroids are similar to rhyolites, they differ in oriented matrix and phenocrysts of quartz, feldspar (potassic feldspar and/or albite) and pseudomorphs of biotite, rarely amphibole. The ratio of phenocrysts to matrix is variable. The composition of matrix has

great involvement in petrographic variability of porphyroids and it comprises small grains of feldspar, quartz with variable amount of metamorphic biotite, chlorite, sericite and ore minerals. As regards the accessory minerals, the Fe-Ti oxides, zircon, tourmaline, monazite and allanite are relatively abundant. Starting rocks of porphyroids were mostly acid volcaniclastics although tectonically deformed metarhyolites sometime indiscernible from metavolcaniclastics are included to them. Also the petrographic criteria for the separation of former tuffs from tuffaceous rocks as were presented by Kamenický (1954) or Chmelík & Snopko (1961) are rather problematic.

Identification of some specific petrographic features related to the alkaline hydrothermal metasomatism is difficult due to the multi-stage character of metamorphic alteration. K-metasomatized rocks contain phenocrysts composed of K-feldspar, chess-board albite or both frequently in complicate successive relations (Fig. 2A-B). Albite phenocrysts are typical for Na-metasomatized rocks. Originally glassy dacites, which experienced the most intensive transformations by alkali metasomatism do not display any specific petrographic features (Fig. 2C-F). It cannot be excluded that formation of metamorphic biotite, which belongs to the oldest metamorphic transformations of studied rocks is directly connected to K-metasomatism. Volcaniclastic rocks with relatively high content of biotite and muscovite are brown-black in colour and they usually contain impregnation by sulfide minerals as pyrite, sphalerite or galena (Fig. 3A-B). Na-metasomatized grey-black varieties with albitized phenocrysts contain chlorite and abundant impregnation of magnetite. Varieties rich in chlorite and/or phengitic muscovite as well as the strong silicified ones were formed as the product of alteration of rocks with biotite during further metamorphic stages. In the vicinity of sulfide-siderite veins increasing amount of sericite, quartz and carbonate is formed at the expense of chlorite and partly also of feldspar (Gubač, 1977; Ivan & Stettner, 1987).



**Fig. 3.** Back scattered electron images (BSE) of acid volcaniclastic rock intensively altered by K-metasomatism. **A:** deformed crystalloclastic structure of the original rhyolite tuff with prevailing quartz (Qz) crystalloclasts and relic orthoclase (Or) crystalloclasts partly replaced by albite. Fine-grained aggregate of muscovite (Ms) together with biotite (Bt) flakes are replacing the original groundmass. **B:** crystalloclast of orthoclase (Or) with metamorphic biotite (Bt) concentrated in strain shadows is partly replaced by albite (Ab) and sphalerite (Sp).

#### 4. USED DATA

To the study of alkaline hydrothermal-metasomatic alteration processes in the acid metamorphosed volcanites and volcanoclastics (porphyroids) from the Gelnica Group, mainly in terms of the major elements (plus zirconium) behaviour during alteration processes, we compiled and summarized all existing and accessible whole-rocks analyses of these rocks. Data from Ivanička et al. (1978), Chmelík & Snopko (1979), Dianiška et al. (1985), Gargulák (1988), Faryad (1991<sup>b</sup>), Vozárová & Ivanička (1993), Hovorka & Méres (1997), Vozárová et al. (2010) as well as unpublished analyses of P. Ivan, were included in the database.

Most of the whole-rock analyses were performed by the classical wet method combined with AAS method (Geologický prieskum, Spišská Nová Ves, Slovakia). The analyses from Vozárová et al. (2010) and a part of the unpublished analyses were performed by the ICP-OES/ICP-MS methods (Acme Labs., Canada), the INAA method (Mega, Stráž pod Ralskem, Czech Republic) was applied for analysing trace elements in a part of the unpublished analyses as well.

A specific set of diagrams for the geochemical study of hydrothermal alteration processes (summarized e.g. by Piercey, 2009) were applied in this work. These diagrams are focused on the identification and quantification of elements mobility as well as the trends of mineral composition changes. We concentrated here mainly on major element mobility, so authentic diagrams by Hughes (1972), Large et al. (2001), Hallberg

(2003) or Davies & Whitehead (2006) were used. Two specific indexes – Hashimoto alteration index (A.I.; Ishikawa et al., 1976) and chlorite-carbonate-pyrite index (C.C.P.I.; Large et al., 2001) – were also applied to study. A.I. =  $100(K_2O+MgO)/(K_2O+MgO+CaO+Na_2O)$ , was defined by Ishikawa et al. (1976) to quantify the intensity of sericite and chlorite alteration that occurs in the footwall volcanics proximal to Kuroko deposits. The main reactions indicated by the index involve the breakdown of sodic plagioclase and volcanic glass and their replacement by sericite and chlorite. Chlorite-carbonate-pyrite index defined as  $C.C.P.I. = 100 * (Fe_2O_3^T + MgO) / (Fe_2O_3^T + MgO + K_2O + Na_2O)$  reflects the formation of mafic hydrosilicates or Mg-Fe carbonates.

The ternary diagram  $MgO-Na_2O-K_2O$  (Hallberg, 2003) was evolved especially for the study of varieties in the hydrothermal-metasomatic alteration of the acid volcanic and volcanoclastic rocks in the Bergslagen area (Sweden). It is fully applicable also for the rocks from the Gelnica Group due to similarity of both areas.

All studied samples of metamorphosed acid volcanic and volcanoclastic rocks from the Gelnica Group were classified into three groups: (1) metarhyolites and metadacites, (2) acid metavolcanoclastics of the psammitic facies (porphyroids) and (3) indiscriminated rocks where all samples without detailed petrographic specification were included. For the greater clarity of the map of alkali metasomatism within the volcanogenic complexes of the Gelnica Group (Fig. 1) there only set of representative samples could be plotted.

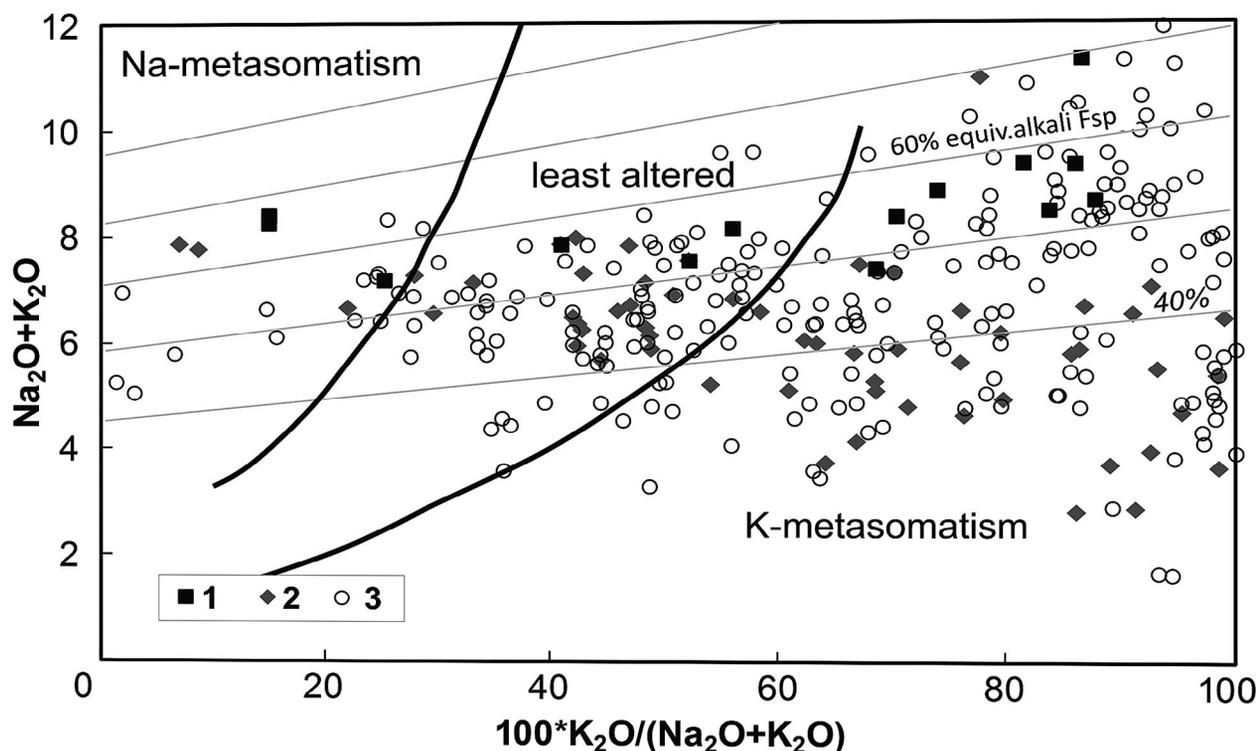


Fig. 4. Identification of hydrothermal-metasomatic alteration processes in the metamorphosed acid volcanics from the Gelnica Group as deviation from the normal magmatic content of alkalis in the diagram by Hughes (1972). Predomination of K-metasomatic alteration is obvious. Explanation of symbols: 1 – acid metavolcanics, 2 – acid metavolcanoclastics of psammitic facies (porphyroids), 3 – undifferentiated metamorphosed acid volcanic and volcanoclastic rocks. Alkali Fsp – alkali feldspar.

**Tab. 1.** Selected whole-rock analyses of acidic metavolcanics and metavolcaniclastics of the Gelnica Group (samples representative for hydrothermal-metasomatic alteration) Explanations: 1 – K-metasomatized dacite, 2 – Na-metasomatized dacite, 3-7 – K-metasomatized rhyolites, 8 – unmetasomatized rhyolite, 9 – K-metasomatized rhyolite tuff; MD – metadacite, MR – metarhyolite, MT – rhyolite metatuff, LOI – loss on ignition, \*stands for H<sub>2</sub>O\*. Laboratories: 2, 4, 5 – Acme Ltd.; 1, 3, 7, 8, 9 – Geol. Prieskum/Mega (see the chapter “Used data”). Data sources: 1-3 – Ivan, original data, 4-5 – Vozárová et al., 2010, 5-9 – Hovorka & Méres, 1997.

	1	2	3	4	5	6	7	8	9
	MD	MD	MR	MR	MR	MR	MR	MR	MT
	BSL-85	FD-484	BSL-38	GZ-2	GZ-6	83/215.2	70/199.4	55/234.2	85/209.7
<b>wt. %</b>									
SiO <sub>2</sub>	62.77	69.56	73.62	76.19	73.91	68.21	70.37	70.57	77.49
TiO <sub>2</sub>	0.57	0.63	0.12	0.07	0.07	0.42	0.48	0.51	0.21
Al <sub>2</sub> O <sub>3</sub>	17.21	16.84	14.00	12.74	12.13	15.13	13.69	15.13	11.70
Fe <sub>2</sub> O <sub>3</sub> t	2.87	1.64	0.30	1.22	1.15	1.99	2.07	1.78	1.25
MnO	0.00	0.01	0.00	0.01	0.02	0.01	0.01	0.20	0.01
MgO	0.36	0.34	0.14	0.18	0.39	0.54	0.86	0.50	0.38
CaO	0.04	0.46	0.07	0.02	0.21	0.51	0.08	1.54	0.01
Na <sub>2</sub> O	0.42	7.08	1.52	1.02	0.56	1.08	0.28	4.30	0.10
K <sub>2</sub> O	13.52	1.92	9.80	7.91	9.23	10.02	9.85	4.01	7.89
P <sub>2</sub> O <sub>5</sub>	0.08	0.12	0.03	0.03	0.03	0.11	0.10	0.12	0.03
LOI	1.38	1.3	0.25	-	-	1.13*	1.72*	1.02*	1.02*
Sum	99.22	99.90	99.86	99.39	97.70	98.03	97.79	98.66	99.07
<b>ppm</b>									
Rb	144	62.4	139	169.2	165.8	145	181	119	148
Cs	3.2	2.6	3.1	3.3	2.7	4.1	15.6	2.3	3.1
Sr	70	35.3	-	48.5	12	-	-	-	-
Ba	940	458	760	360.6	292	1670	1830	815	515
Zr	187	136.9	80	84.6	74.5	220	273	274	146
Y	21	24.1	43	43.6	41.4	-	-	-	-
Hf	6.6	4.0	4.6	3.7	3.6	5.10	5.30	6.20	4.10
Th	9.5	7.7	13.3	20	23.1	14.2	7.5	12.7	13.2
Ta	0.78	0.6	0.6	1.1	1.2	0.8	0.71	0.8	0.74
Nb	-	5.9	7.7	7.2	-	-	-	-	-
Sc	24.5	92	-	-	-	13.1	22.9	14.7	7.4
La	32.5	18.3	34	16.3	27.5	34	25.9	32.5	27.9
Ce	64	51.5	70	36.6	55.7	80	58	78	64
Pr	-	6.97	-	4.16	7.3	-	-	-	-
Nd	26.6	27.7	25.2	16.1	26.6	39	29.1	42	33.5
Sm	5.6	5.36	6.8	4.1	6.18	6.10	5.50	5.90	6.20
Eu	0.86	1.25	0.79	0.14	0.22	0.81	1.50	1.05	0.78
Gd	-	5.17	-	5.16	6.28	6.80	6.80	6	5.90
Tb	0.58	0.75	1.1	1.18	1.13	0.93	0.87	0.97	0.81
Dy	-	4.36	-	7.67	6.16	-	-	-	-
Ho	-	0.90	1.8	1.56	1.55	-	-	-	-
Er	-	2.58	-	4.87	4.21	-	-	-	-
Tm	0.55	0.35	0.64	0.76	0.67	0.41	0.63	0.3	0.43
Yb	1.95	2.31	3.6	4.88	3.96	3.40	3.20	2.7	3.10
Lu	0.51	0.33	0.71	0.68	0.62	0.58	0.64	0.5	0.49

## 5. GEOCHEMISTRY

A persuasive indicator of the fact, that contents of the alkalis in the studied samples do not correspond as a rule with the original composition of rocks formed during crystallization, is their positions in the diagram on the Fig. 4. A considerable amount of samples fall outside the field for magmatic rocks what is generally ascribed to the effects of K- and Na-metasomatism, respectively. Among studied samples those with the attributes of K-metasomatism predominate.

Representative chemical analyses of acid volcanic rocks which experienced potassic or sodic metasomatic alterations are presented in Tab. 1. The highest concentrations of alkalis display metavolcanic rocks originally represented by glassy dacites (analyses 1 and 2), high concentrations are typical also for metarhyolites (analyses 3-8) where  $K_2O$  content can exceed 10 wt. %. Concentrations of K and Na in unaltered metarhyolites are practically equal and vary around 4 wt. % (analysis 9). Concentrations of alkalis in the metasomatized acid volcanics (porphyroids; analysis 10) vary in wide span, but generally are lower than in rhyolites (Fig. 4).

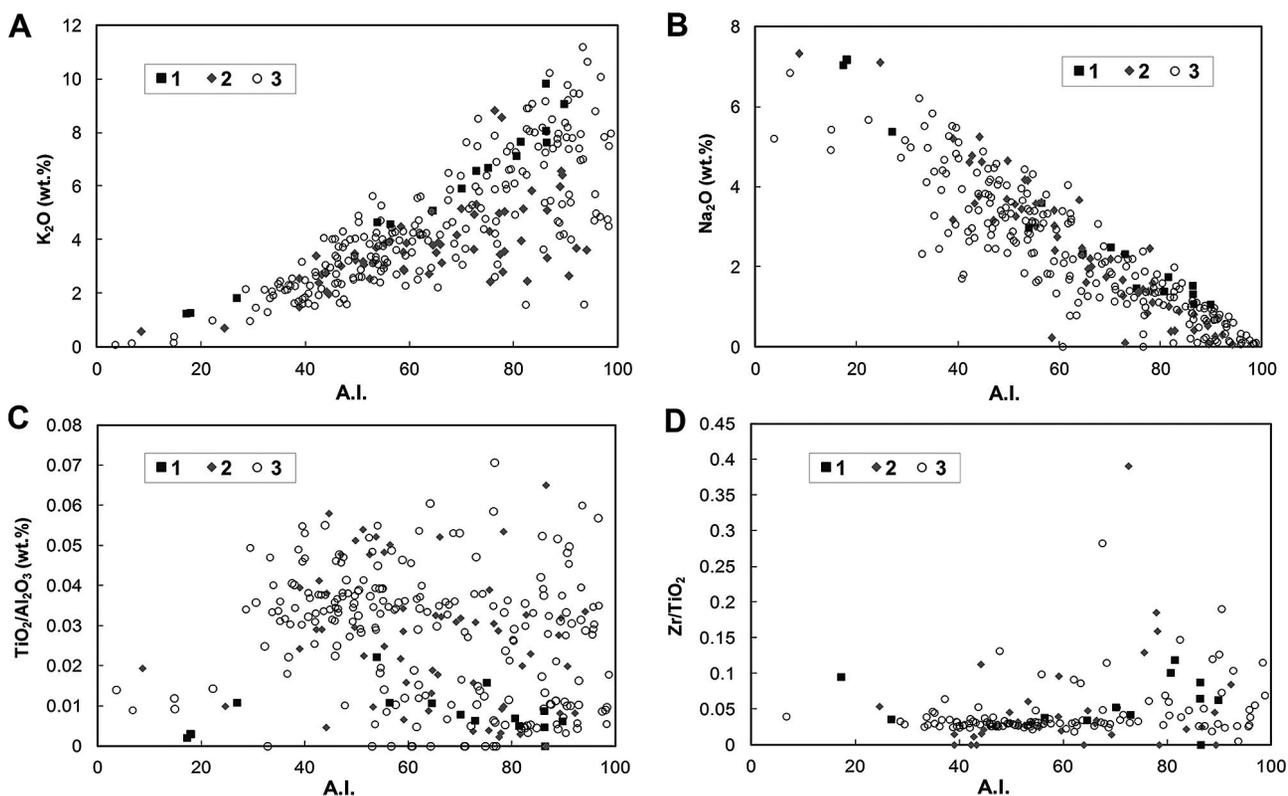
The  $K_2O$  contents in the studied metamorphosed acid volcanic rocks correlate very well with the Hashimoto alteration index (A.I.), the same correlation, but negative in sense, is well visible also for  $Na_2O$  values (Fig. 5A-B). No correlation between A.I.

and  $TiO_2/Al_2O_3$  ratio (Fig. 5C) is supporting generally accepted the least mobility of Ti and Al in hydrothermal-metasomatic processes among all major elements. A similar picture provided the A.I. vs.  $Zr/TiO_2$  plot (Fig. 5D), where Zr represents relatively immobile element as well.

A more detailed specification of involved alteration types, especially regarding newly formed mineral associations in the studied rocks, allows A.I. vs. C.C.P.I. alteration box plot (Fig. 6). Relatively small part of samples only lies within the field of unaltered rhyolite volcanics. Most of them plot within the field of potassic feldspar and weak or strong sericite alteration respectively.

A more complex view at the alteration of studied rock types gives the  $MgO-Na_2O-K_2O$  ternary plot on the Fig. 7. The samples of metarhyolites and porphyroids fall mainly into the field for potassic alteration, to a lesser degree into the fields for unaltered to weakly Na- as well as Mg-altered felsic metavolcanics.

The  $K_2O/Al_2O_3$  vs.  $Na_2O/Al_2O_3$  and  $K_2O/Al_2O_3$  vs.  $MgO/Al_2O_3$  plots expressed in molar ratios (Davies & Whitehead, 2006) have most of the projection points concentrated mainly along the albite-muscovite or albite-potassic feldspar composition trends in the first diagram (Fig. 8A), and under the line connecting the low Mg chlorite and muscovite or at both sides of this line at low values of  $MgO/Al_2O_3$  in the second case (Fig. 8B).



**Fig. 5.** Variation trends of the Hashimoto alteration index (A.I.) related to (A)  $K_2O$ , (B)  $Na_2O$  (C)  $TiO_2/Al_2O_3$  and (D)  $Zr/TiO_2$  within studied rocks (Symbols: see Fig. 4). Very good correlation between  $K_2O$  and A.I. together with similarly good but reversed correlation between  $Na_2O$  and A.I. indicate continuous character of the hydrothermal-metasomatic alteration as regards its intensity and direction (breakdown of sodic plagioclase and volcanic glass and their replacement by sericite and chlorite). Absent correlation between A.I. and  $TiO_2/Al_2O_3$  and  $Zr/TiO_2$  ratios respectively is a manifestation of the immobility of these elements during the studied alteration.

Although mobility of trace elements during alkali metasomatism is beyond the scope of this paper, it is worth of mentioning that the preliminary data indicate immobile behaviour of REE and HFSE (cf. Ivan & Méres, 2005). On the other hand high mobility is typical for Rb, which concentrations highly positively correlate with  $K_2O$  contents (not shown). Due to this fact diagrams using this element for discrimination of tectonic setting of the acid volcanic rocks do not yield relevant results. Intensive formation of biotite and muscovite related locally to K-metasomatism of the acid volcanics seems to be accompanied by mobility of metals (Zn, Pb, Cu; Fig. 3AB).

## 6. DISCUSSION

The geochemical testing of 293 analyses of metamorphosed acid volcanic rocks and their volcanoclastics (porphyroids) from the Early Paleozoic Gelnica Group in the Gemeric Superunit showed that the content of some elements, especially alkalis, is modified by the subsolidus metasomatic alteration of the regional extent. The predominantly potassic character of metasomatism is obvious from the Hughes plot (1972) (Fig. 4). Concentrations of alkali elements are equivalent to 45–65 % of alkali feldspar content in the most cases. The highest concentration of alkali elements is related to altered rocks represented originally by the glassy dacites (13.52 wt. %  $K_2O$  and 7.08 wt. %  $Na_2O$  respectively; Tab. 1 and Fig. 2C-F).

Very good correlation observed between  $K_2O$  and A.I. together with similarly good but reversed correlation between  $Na_2O$  and A.I. indicates continuous character of the

metasomatic alteration as regards its type and intensity (Fig. 5A-B). The intersection of both trends close to 4 wt. % should roughly match the original contents of alkalis within the studied rocks, what is in agreement with the previous findings of Ivan & Méres (2005) about high-potassic calc-alkaline (definitely not alkaline) primary character of metarhyolites. Close correlation between alkalis and A.I. reflect formation of new minerals containing Na or K at the expense of the original mineral association during the metasomatic alteration. So A.I. can be accepted as relatively reliable indicator of alkali metasomatic alteration mostly in effusive volcanic rocks. Greater variability of  $K_2O$  content at higher values of A.I. which is visible among metavolcanoclastics could be result of primary variability in feldspar content and/or variable feldspar/mica ratio in the alteration products. Absence of correlation between A.I. and  $TiO_2/Al_2O_3$  ratio (Fig. 5C) indicates immobility of Ti and Al over a period of alkali metasomatism. Scattered values of  $TiO_2/Al_2O_3$  ratio mainly in metavolcanoclastics reflect variable content of quartz in relation to Al-silicates contents and/or also possible admixture of less evolved volcanic material.

The  $MgO-Na_2O-K_2O$  diagram (Hallberg, 2003) supports above mentioned findings that substantial part of the studied acid volcanic and volcanoclastic rocks from the Gelnica Group experienced K-metasomatic alteration, although relatively extensive is also fraction of less altered rocks (Fig. 7). Unlike the situation in the Bergslagen area in Sweden, the Mg-metasomatism manifestations are less distinctive and Na-Mg-metasomatism almost absent. For the present it cannot be excluded that the cause is related to the selection bias in sampling.

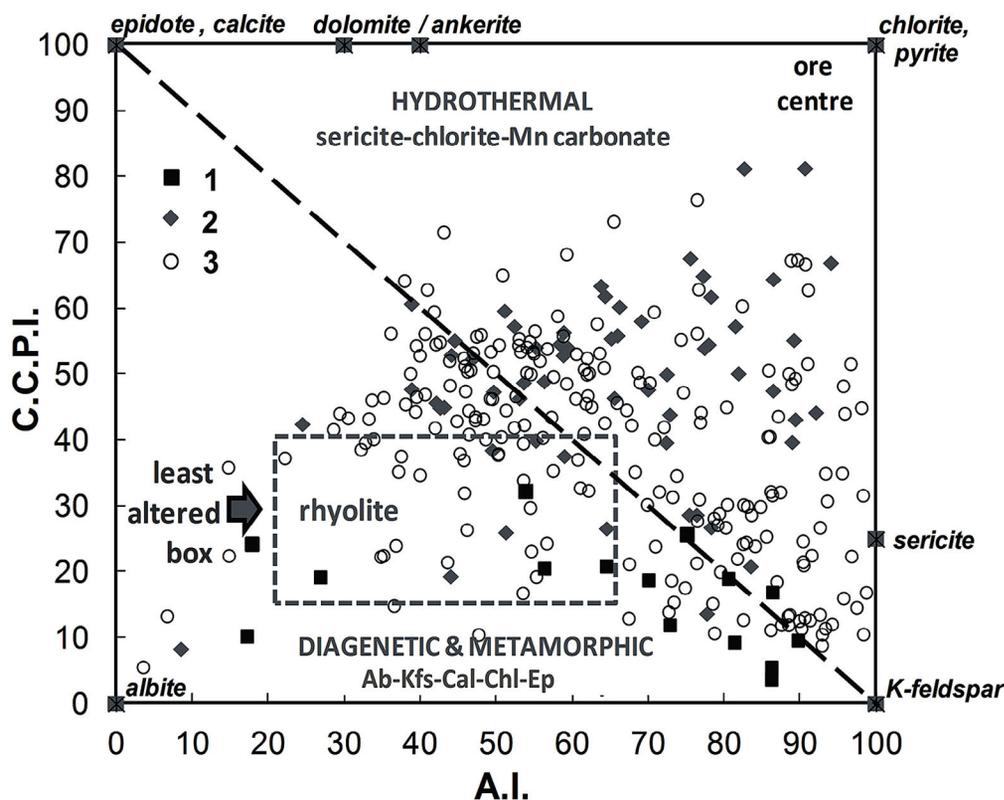


Fig. 6. Alteration box plot based on variations of the Hashimoto alteration index (A.I. by Ishikawa et al., 1976) vs. the chlorite-carbonate-pyrite index (C.C.P.I.; index and diagram was taken from Large et al., 2001). Diagram contains a box for the least altered rhyolites according to Large et al. (2001) as well as nodes for individual alteration minerals (Symbols: see Fig. 4, Ab – albite, Kfs – K-feldspar, Cal – calcite, Chl – chlorite, Ep – epidote). It is obvious that majority of studied rocks experienced hydrothermal-metasomatic alteration which leads mostly to the increase of K-feldspar and/or sericite contents, whereas formation of chlorite, amphibole, biotite and/or pyrite respectively explains observed compositions only for the minor part of studied samples.

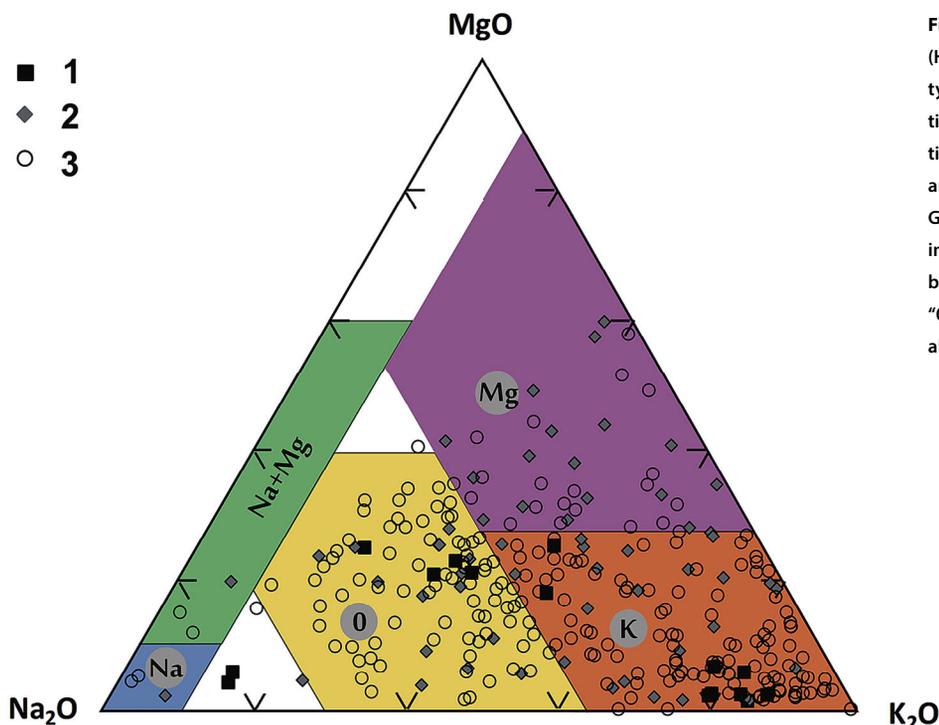


Fig. 7. Ternary MgO-Na<sub>2</sub>O-K<sub>2</sub>O plot (Hallberg, 2003) for the identification of type of hydrothermal-metasomatic alteration which transformed chemical compositions of acid metamorphosed acid volcanic and volcanoclastic rocks from the Gelnica Group (Symbols: see Fig. 4). The diagram indicates the presence of Mg-alteration besides the Na- and K-alteration. Symbol "O" in the diagram labels the field of weakly altered samples.

Changes of the mineral composition of acid volcanic and volcanoclastic rocks in relation to alkali metasomatism could be interpreted from the alteration diagram by Large et al. (2001) (Fig. 6) as well as alkali-alumina molar diagram by Davies & Whitehead (2006) (Fig. 8). It seems to be evident, that K-metasomatic alteration is a result of the replacing of primary plagioclase (and possibly volcanic glass too) mainly by K-feldspar and/or muscovite/sericite and biotite. Some muscovite/sericite was created secondary at the expense of the metasomatic K-feldspar as a product of tectonothermal or hydrothermal alterations. Na-metasomatism is related to formation of albite. The projection of

many acid metavolcanic rocks closely above the box of the least altered rocks in the A.I. vs. C.C.P.I. diagram (Fig. 6) could be caused by the admixture of less evolved volcanic material. Majority of chlorite probably originated secondarily at the expense of biotite as a result of further metamorphic and hydrothermal alterations.

Spatial distribution of acid volcanic and volcanoclastic rocks altered by alkali metasomatism (Fig. 1) indicates that K- and Na-metasomatized rocks are located in the separate areas. A part, but not all of Na-metasomatites is clearly related with contact zones of the Permian small granitoid bodies (granitoid body

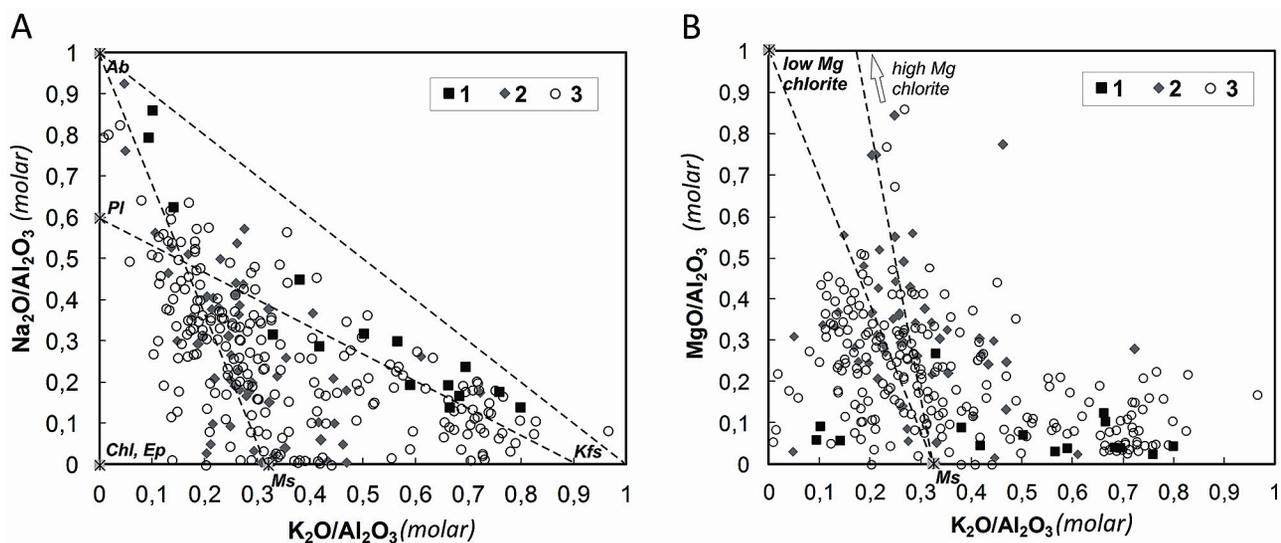


Fig. 8. Alkali-alumina molar ratio plots (Davies & Whitehead, 2006) for the acid metavolcanics and metavolcaniclastics from Gelnica Group. A) K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> vs. Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> indicates that the primary plagioclases (and volcanic glass possibly) were substituted mainly by K-feldspar. B) K<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> vs. MgO/Al<sub>2</sub>O<sub>3</sub> displays weak negative correlation between MgO and K<sub>2</sub>O interpreted as the result of chlorite/sericite conversion. (Symbols: see Fig. 4, Ab – albite, Pl – plagioclase, Chl – chlorite, Ep – epidote, Ms – muscovite, Kfs – K-feldspar).

near Zlatá Idka; cf. Dianiška, 1983). Prevailing K-metasomatites seem to mostly form compact areas without the unmetasomatized rocks, which could reflect spatially localized mode of the hydrothermal solution flows. The age of alkali hydrothermal-metasomatic alteration remains indeterminate mainly due to possibility discussed below, that there could be more than one stage of this process.

The similarity in the starting rocks and geochemical character of alkali metasomatism as well between the Gelnica Group and Bergslagen area (cf. Lagerblad & Gorbatshev, 1985; Hallberg, 2003) allowed us to formulate following genetic assumptions for the Gelnica Group: (1) The main phase of alkali metasomatism represents the oldest subsolidus alteration, probably related to Ordovician, which is also the age of acid volcanism (Vozárová et al., 2010) generated in the arc setting (Vozárová & Ivanička, 1996; Ivan & Méres, 2005) ergo in environment with high thermal gradient. Spatially widespread metasomatic mineral association with biotite, which is locally superimposed by all tectonothermal/hydrothermal alterations evolved along the fault zones or hydrothermal vein structures, seems to be support this timing. (2) The alkali metasomatism was probably caused by the infiltration and circulation of sea water induced by local thermal anomalies connected to magmatic bodies. (3) The areas with predominating Na-, K- or Mg-metasomatism represent different parts of the original hydrothermal system, where the K-metasomatism was probably its lower temperature section. (4) From the distribution of monazite U-Pb ages follows, that except Lower Ordovician two other thermal events took place in the Gelnica Group during the Paleozoic time (Vozárová et al., 2014); (a) in the Upper Silurian/Lower Devonian and (b) in the Permian. The former was probably caused by the rift-related basaltic magmatic activity mostly in the form of small subvolcanic bodies (Ivan, 2009), the later by small intrusions of S-type granites (Finger & Broska, 1999). Probably only Na-metasomatism restricted on the proximate vicinity of the magmatic bodies is related with both thermal events. (5) Alkali metasomatism in the acid metavolcanics and metavolcaniclastics of the Gelnica Group is clearly overprinted by the hydrothermal-metasomatic alteration which occurs along with the siderite-sulfide and quartz-stibnite veins of Alpine (probably Lower Cretaceous) age (Hurai et al., 2008). Biotite is chloritized and then replaced by sericite and carbonate, feldspar is replaced by carbonate, sericite or quartz (Varček, 1965; Gubač, 1977; Ivan & Stettner, 1987). (6) At many places the hydrothermal system associated with extended alkali metasomatism is able to produce ore mineral deposits (e.g. Hollocher et al., 1994; Barriga & Fyfe, 1998; Piercey et al., 2008). Within Bergslagen area the existence of such a hydrothermal system is connected to stratiform deposits of Cu, Pb, Zn sulfides, Fe and Mn oxides subsequently altered to various types of skarns (Lagerblad & Gorbatshev, 1985; Stephens et al., 2009). These types of deposits are present in the Gelnica Group as well (Grecula et al., 1995). Base metal sulfide impregnations formed locally as a by-product of the intensive alkali metasomatism (Fig. 3A-B) could serve as a metal source for the younger siderite-sulfide vein deposits.

## 7. CONCLUSIONS

The acid metavolcanics and metavolcaniclastics within Gelnica Group were subjected to extensive alkaline hydrothermal-metasomatic alteration. K-metasomatism was related to formation of K-feldspar, less biotite and muscovite at the expense of original matrix and feldspar phenocrysts, whereas Na-metasomatism manifested itself by formation of albite. Alkaline metasomatism seems to be the oldest subsolidus alteration of acid volcanic and volcanoclastic rocks connected to their Early Paleozoic geological history. An extensive hydrothermal system related with metals mobility could be responsible for this type of alteration, where K-metasomatism could be produced in its lower thermal parts. This hydrothermal system might be linked to polymetallic stratiform mineralization within Gelnica Group as well as it could serve as the pre-concentrator of metals for sulfide-siderite veins.

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