

Geochemistry of hydrothermally altered rocks from the Asarel porphyry copper deposit, Central Srednogie

Atanas Hikov

*Geological Institute, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 24, 1113 Sofia, Bulgaria;
e-mail: ahikov@geology.bas.bg*

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Abstract. The distribution of major and trace elements in hydrothermal alteration zones (propylitic, argillic, sericitic and advanced argillic) from the Asarel porphyry copper deposit is studied. Strontium was found to demonstrate the most characteristic behaviour among all studied elements – it is depleted from propylitic, argillic and sericitic rocks and concentrates in advanced argillic rocks where it is included in alunite and APS minerals. Manganese, Co, Ni, Zn, Cs, Y, MREE and HREE are strongly mobile and are depleted with increasing of alteration degree, while Rb concentrates in sericitic rocks. Titanium, Zr, V, Ta, Nb, Th, U and LREE have inert behaviour during alteration. Alunite, APS minerals and rutile are the minerals that control the geochemistry of trace elements in the zones of advanced argillic alteration.

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Key words: trace elements, hydrothermal alteration, advanced argillic alteration, alunite, APS minerals, Asarel porphyry copper deposit.

INTRODUCTION

Among all hydrothermal-metasomatic processes the advanced argillic alteration (Meyer, Hemley, 1967) or its analogues in the genetic classification of metasomatites “secondary quartzites” (Zharikov, Omel’yanenko, 1978) are widespread in Bulgaria. More than 30 occurrences of advanced argillic alteration are known (Velinov et al., 2007). They are concentrated mainly in the Srednogie Zone and in the Central and Eastern Rhodopes. Part of them is associated with porphyry copper and epithermal deposits, sometimes being raw material as well. These circumstances could explain the deep interest in this hydrothermal alteration type, its relation with the ore-forming processes and definition of criteria for prognosis and prospecting of above mentioned and new ore deposits.

The occurrences of secondary quartzites (advanced argillic altered rocks) in Bulgaria are well studied in petrological, mineralogical and structural aspects (Velinov et al., 2007). Some problems of the theory such as physicochemical conditions during their

formation and classification of the metasomatites were also discussed (Kanazirski, 2011). The geochemistry of these altered rocks is less studied. There are some investigations of the geochemistry of the ore elements and some accompanying elements in the alteration zones because of the close connection between ore deposition and hydrothermal alterations (Pliushchev, Shatov, 1985; Fragova et al., 1987). The behaviour of a single element or a group of elements during hydrothermal alteration was also studied (Radonova, Karadjova, 1974; Velinov et al., 1975; Chipchakova et al., 1981; Yordanov, Kunov, 1987), including hydrothermal alteration in Asarel porphyry copper deposit (Radonova, Karadjova, 1974; Hikov, 1992).

The aim of the present study of hydrothermally altered rocks from the Asarel porphyry copper deposit is to give a more detailed view on the geochemistry of advanced argillic alteration and accompanying alteration types. A considerable number of major and trace elements has been analysed, and their behaviour from the non-altered to the most intensively altered rocks was followed. The geochemical analyses are

combined with mineralogical studies on the common phases (e.g. alunite group minerals) in the advanced argillic altered zones to explain which minerals may concentrate the elements of interest. The study of the distribution of trace and major elements in different alteration types will help us (i) to better understanding of the processes that lead to the advanced argillic alteration; (ii) to outline typical elements and element ratios that can be used as exploration criteria; and (iii) to make a link to the ore deposition as a related process.

GEOLOGICAL SETTING

The Asarel porphyry copper deposit is located in the Panagyurishte ore region, Central Srednogorie (Fig. 1). The ore region is a part of the Late Cretaceous Apuseni–Banat–Timok–Srednogorie (ABTS) magmatic and metallogenic belt (Popov et al., 2000b) which is one of the largest metallogenic belts in Eastern Europe (Bogdanov, 1977; Vassileff, Stanisheva-Vassileva, 1981). The ABTS belt is resulted from subduction of Tethyan oceanic crust under the European continental

margins that generated the Upper Cretaceous volcano–plutonic complexes and associated ore deposits (Boccaletti et al., 1974; Dabovski et al., 1991; Berza et al., 1998; Popov et al., 2000b; Lips, 2002; von Quadt et al., 2005).

The Panagyurishte ore region is situated in the central part of the Srednogorie Zone and is characterized by development of intensive Late Cretaceous magmatism (Dabovski et al., 2002). High-K calc–alkaline to shoshonitic series predominate while calc–alkaline ones occur only in the central part (Dabovski et al., 1991; Kamenov et al., 2007). Many porphyry copper and Cu–Au epithermal deposits are discovered in the region (Popov et al., 2003). The age of magmatism is between 92 and 78 Ma while that of Cu–Au deposit formation in the northern and central parts is from 92 to 86 Ma (von Quadt et al., 2005).

The Asarel magmatic center (Nedialkov et al., 2006, 2007) is located 7 km NW of the town of Panagyurishte. It represents a volcano–plutonic edifice situated in the easternmost part of the Asarel volcanic stripe (Asarel effusive Formation, according to Popov et al., 2012),

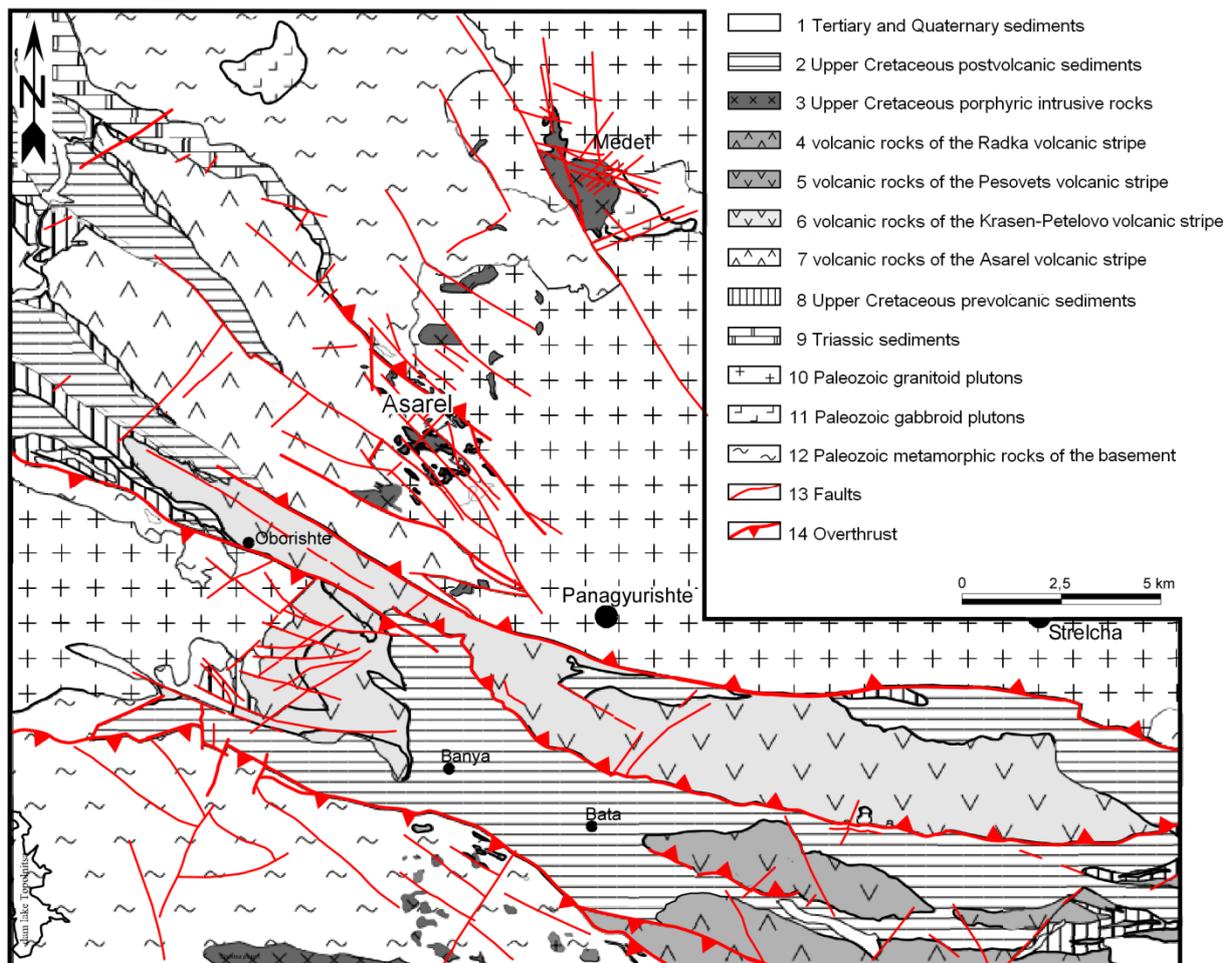


Fig. 1. Geological sketch map of part of the Panagyurishte ore region with Asarel porphyry copper deposit (after Nedialkov et al., 2007).

a part of so-called NW orientated Asarel graben-syncline (Angelkov, 1973; Ignatovski, 1979). The Paleozoic basement is represented by metamorphic (biotite and two-mica gneisses, amphibolites, slates) and granitoid rocks from the Smilovene pluton (Katzkov, Iliev, 1993; Nedialkov et al., 2007). The volcanic activity successively formed: 1) andesites to latites; 2) basaltic andesites; 3) andesites to dacites. The volcanics and Paleozoic granitoids are intruded by comagmatic porphyritic plutons of 3 impulses: 1) quartz-diorite to quartz-monzodiorite porphyry; 2) quartz-diorite, quartz-monzonite to granodiorite porphyry; 3) granite porphyry (simultaneous to post ore) (Zartova et al., 2004; Nedialkov et al., 2006, 2007). U-Pb zircon ages of the Asarel magmatic rocks are between 89.90 ± 0.26 Ma and 89.13 ± 0.22 Ma suggesting a short lived, <1 Ma ore related magmatism (Peytcheva et al., 2007).

Asarel volcanic and porphyritic rocks belong to the calc-alkaline and high-K calc-alkaline series. The geochemical characteristics of trace elements are typical of enriched mantle source and indicate a subduction-related volcanic-arc setting (Nedialkov et al., 2007; Kamenov et al., 2007).

The Asarel volcanic center was described as paleovolcanic edifice of central type (Angelkov, 1973; Angelkov, Parvanov, 1980; Bogdanov, 1980, 1987), as well as of linear type (Ignatovski, 1979). Popov, Petkov (1994) and Popov et al. (1996) considered that the position of volcanic structure is marked by concentration of small subvolcanic bodies and dikes and of radial-concentric fractures. A big volcanic neck was described also in the western part of the deposit. The eastern part of the volcano cone was lifted along the Mialski fault and was entirely eroded.

The porphyry copper ore body is a cone-shaped stockwork with highest metal concentration in the central part (Bogdanov, 1987; Popov et al., 1996). The main hypogene ore stage (quartz + chalcopyrite \pm pyrite) temporally associates with sericitic and transitional sericitic-propylitic alteration (Bogdanov, Bogdanova, 1981; Bogdanov, 1987; Strashimirov et al., 2002). Several mineral assemblages representative of high-sulphidation epithermal style (enargite, goldfieldite, colusite, etc.) are established in the upper levels (Petrunov et al., 1991). They are spatially related to sericitic and advanced argillic alterations of volcanic rocks. Thus, the Asarel deposit combines typical features of porphyry copper mineralization at depth with an overprint of high-sulphidation style of mineralization in the upper parts of the system (Strashimirov et al., 2002). A well-developed supergene enrichment zone is of important economic interest for copper and gold production (Bogdanov, 1987; Strashimirov, 1992). At the beginning of 2006 the remaining resources in Asarel porphyry copper deposit were 186 Mt ore with average grade 0.41% Cu and 0.12 ppm Au (Milev et al., 2007).

ANALYTICAL METHODS

Samples from representative cross-sections in the open pit were collected to study the mineral composition and geochemistry of all alteration types in Asarel porphyry copper deposit. Samples from drillholes (drilled during 1988–1989) were also used. The results from 30 drillholes were presented as unpublished report by Velinov et al. (1989)¹ with the author's participation. Additionally, twelve drillholes were sampled and the results are presented here for the first time.

Detailed study of each sample was made to precisely define the alteration type and its place in the alteration zoning. Mineral composition of altered rocks was examined in thin sections, supported by X-ray diffraction (XRD) and differential-thermal analyses (DTA) at the Geological Institute of BAS, Sofia. Minerals such as alunite, aluminium phosphate-sulphates (APS), etc. were analyzed by electron microprobes at the Geological Institute, Eurotest Control Ltd. (Sofia) and BRGM (Orleans, France).

The chemical composition was studied mainly by X-ray fluorescent (XRF) analyses (for major and for trace elements – Zr, Sr, Rb, Mn, Cr, V, Ti, Ba, rarely Y) and atomic absorption (AA) analyses (for Cu, Zn, Pb, Ni, Co, Li, limited Ga, Ag, Au) at the Geological Institute. Chemical (for P and S) and flame photometric analyses (for K and Na), and occasionally classical silicate analyses were also used. Limited number of samples were analysed for REE by ICP-MS at AcmeLabs Ltd. (Vancouver, Canada) (results for other trace elements were also obtained), by ICP-EOS at the Geological Institute and by radio-chemical analyses at the Institute of Geochemistry (Irkutsk, Russia), where some analyses for F, Cl and Au were made, too.

Stable isotope data on S, O and H were obtained in BRGM (Orleans, France). Finally, whole-rock (2 samples) and in-situ LA-ICP-MS analyses of the minerals rutile and alunite were made at the Geological Institute, BAS. The data on chemical composition of altered rocks from Asarel deposit are presented in Tables 1 and 2.

HYDROTHERMAL ALTERATION

The volcanic and plutonic rocks that host the Asarel deposit were affected by intensive hydrothermal alterations (Radonova, Stefanov, 1974; Ignatovski, 1981; Ignatovski, Tzvetanov, 1981; Bogdanov, 1987; Velinov et al. (1989)¹; Arnaudova et al., 1991; Kanazirski et al., 1993, 1995, 1996, 2000, 2002; Kanazirski, 1996, 2011; Popov et al., 1996, 2000a,

¹ Velinov, I., Kanazirski, M., Gorova, M., Petrunov, R., Hikov, A., Dragov, P., Dimitrova, E., Kunov, A. 1989. *Topomineralogic documentation of the new exploration drillholes from Asarel deposit*. Unpublished report, Geological Institute BAS, 349 pp.

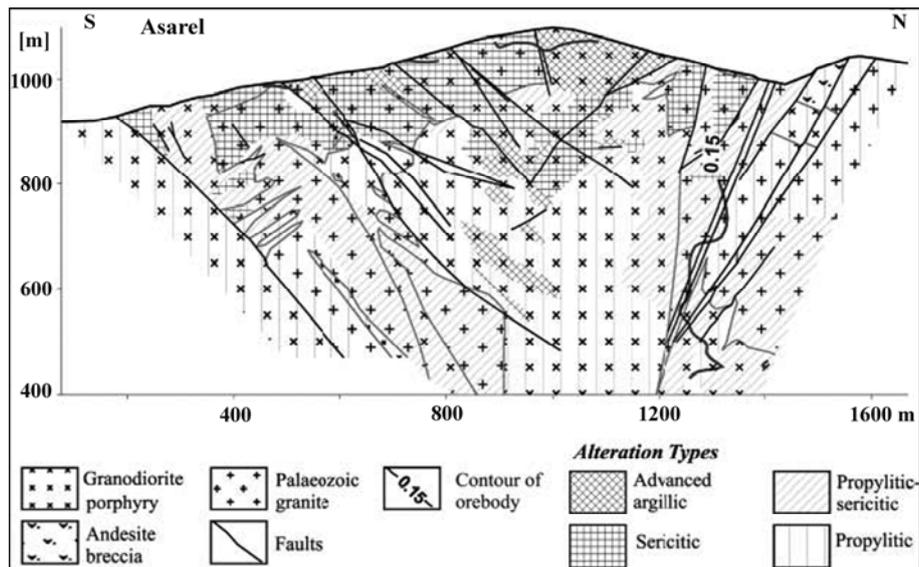


Fig. 2. Geological section through the central part of the Asarel deposit with the main alteration types (after Strashimirov et al., 2002).

2012; Strashimirov et al., 2002). Propylitic, argillic, sericitic and advanced argillic alteration types are established, as well as transitional alteration types – propylite-argillic, propylite-sericitic, argillic-sericitic and sericite-advanced argillic (Popov et al., 1996). Advanced argillic alteration is subdivided in two subtypes: pyrophyllite (acid-chloride) and alunite (acid-sulphate) (Kanazirski, 1996). It is thought that these hydrothermal alterations are related to the end of the effusive stage of the formation of the structure (Arnaudova et al., 1991; Popov et al., 1996). K-silicate (K-feldspar-biotite) early alteration is weakly developed in the deeper part of the system (Bogdanov, 1987; Arnaudova et al., 1991) because it was overprinted by later sericitic and advanced argillic alteration (Popov et al., 1996; Strashimirov et al., 2002). Some K-feldspar-biotite manifestations (small veinlets and filled fracture zones) among propylite altered granodiorite porphyry are observed only once in the open pit (level 915) by the author.

Later pre-ore hydrothermal alterations such as sericitization and silicification, as well as limited argillization and chloritization are not well studied but they are closely related to the ore mineralization (Popov et al., 1996). Calcite-zeolite and anhydrite-gypsum late alterations are defined as post ore (Bogdanov, 1987; Popov et al., 1996).

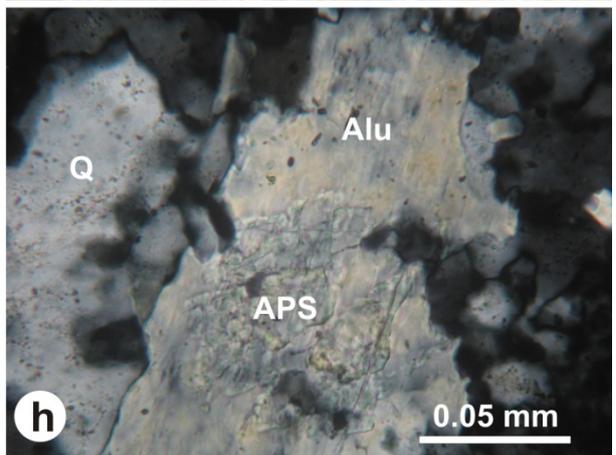
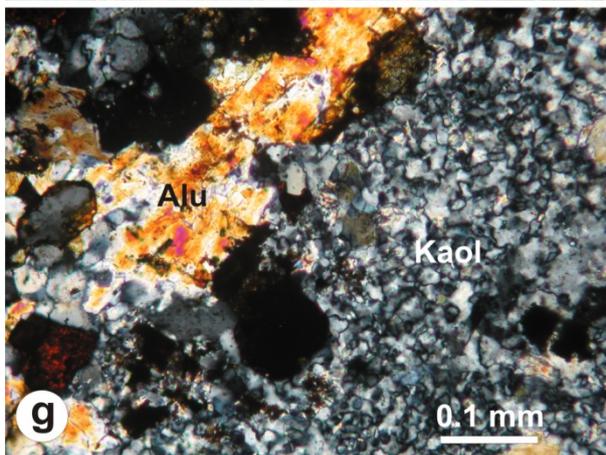
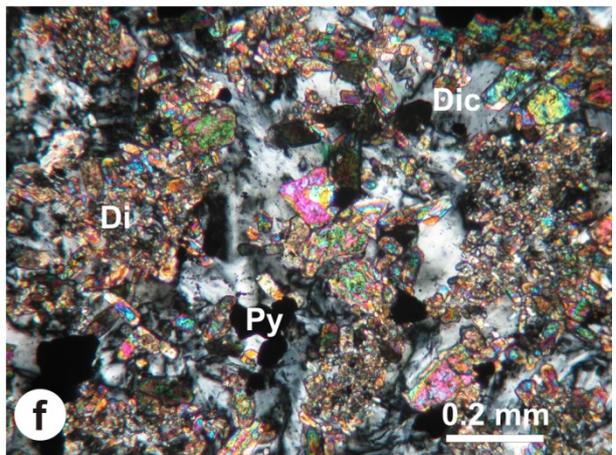
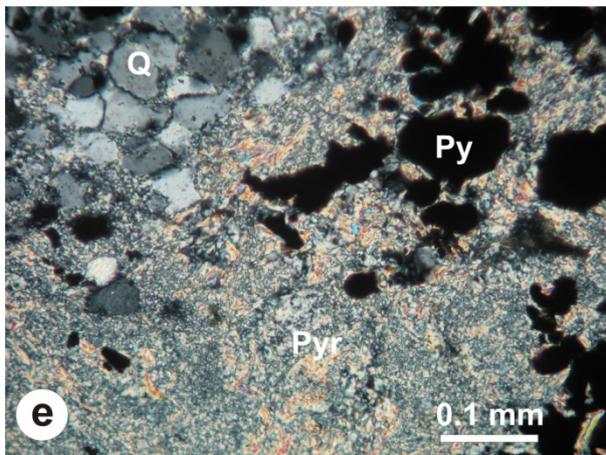
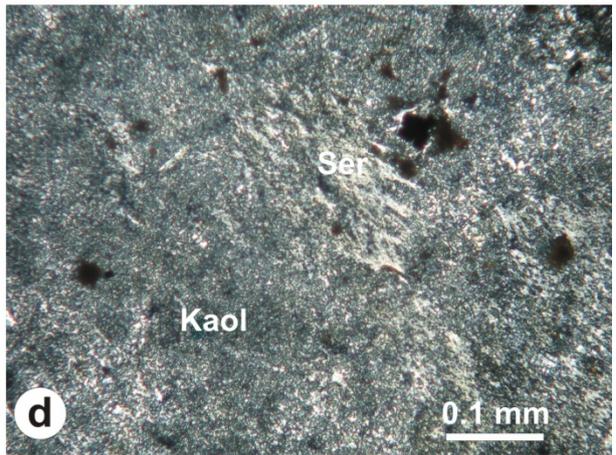
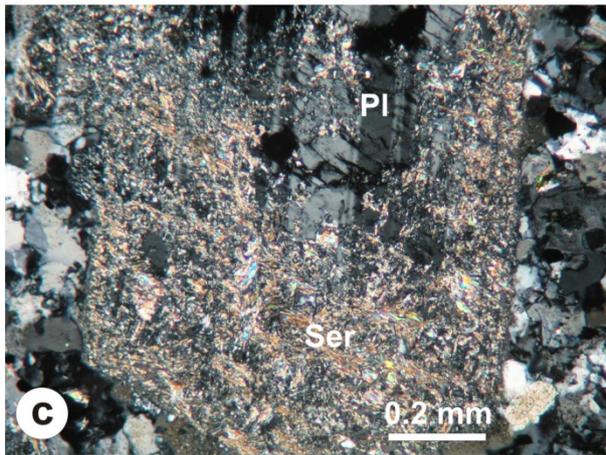
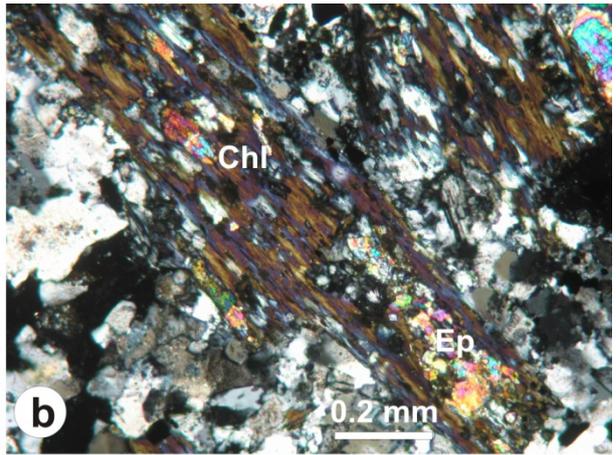
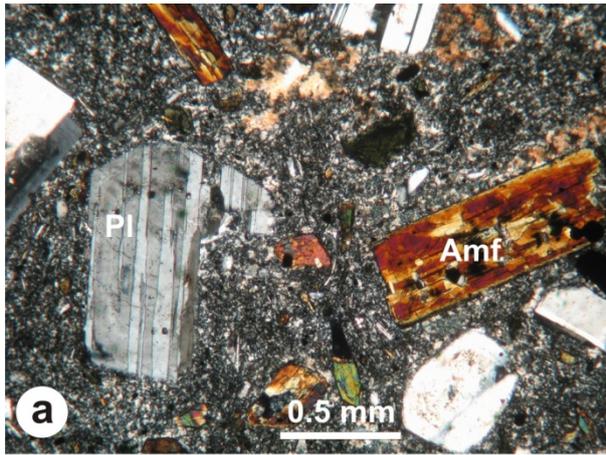
Alteration zoning is expressed by successive development of advanced argillic alteration, sericitization, argillization and propylitization from the center to the periphery and from the top to the bottom of the deposit (Fig. 2). This zoning is highly complicated by differences in the intensity of alteration related to the local zones of different permeability (breccias, rock contacts, different rock types, fractured zones, ore zones, etc.), as well as by the telescopic development of pre-, syn- and post-ore metasomatic and supergene mineral formation (Popov et al., 1996). Altered rocks are result of unified petrogenetic process in the evolution of the Asarel volcano-intrusive-hydrothermal system and are nominated to the secondary quartzite formation and the formation of quartz-sericite metasomatites (Kanazirski et al., 2000).

This study confirms previously described metasomatic rocks in the deposit. Advanced argillic alteration represented by its two subtypes (acid-sulphate and acid-chloride) is a subject of special interest. Ideal mineral composition is alunite + quartz + pyrite for the acid-sulphate subtype and pyrophyllite + quartz + pyrite (Fig. 3e) for the acid-chloride subtype but these cases are rare. The typical association of pyrophyllitic altered type includes also diaspore, dickite, kaolinite,

Fig. 3. Microphotographs of fresh and altered rocks from the Asarel deposit

- a – plagioclase (Pl) and amphibole (Amf) porphyries in unaltered andesite, ×N;
- b – chlorite (Chl) and epidote (Ep) replacing amphibole in propylitic rock, ×N;
- c – sericite (Ser) replacing plagioclase (Pl) in propylitic rock, ×N;
- d – sericite (Ser) and kaolinite (Kaol) in sericite-argillic rock, ×N;
- e – pyrophyllite (Pyr), quartz (Q) and pyrite (Py) in pyrophyllite advanced argillic rock, ×N;
- f – dickite (Dic)-diaspore (Di) advanced argillic rock, ×N;
- g – kaolinite (Kaol)-alunitic (Alu) advanced argillic rock, ×N;
- h – core of APS mineral in alunite (Alu) among quartz (Q), ×N.

→



sericite, rarely alunite, APS minerals, zunyite, barite, while the alunitic type contains kaolinite, APS minerals, zunyite, rarely diaspore, pyrophyllite, sericite, barite (Fig. 3g, h). In fact, disequilibrium mineral associations can be seen in most cases which are due to the frequent changes of fluid composition from acid-chloride to acid-sulphate and *vice versa*. The classification of a given sample to a certain alteration subtype is based on the predominant minerals and is relative to some extent. Very rare are metasomatic rocks with diaspore and/or dickite as predominant minerals (Fig. 3f). In cases where sericite or kaolinite predominates, the other minerals from the alteration association are used to define a sample as advanced argillic or sericitic or argillic altered. The distinguishment of sericitic from intermediate argillic alteration is relative to some extent also because of the significant variations of minerals which define the alteration type (sericite and kaolinite, respectively) and often mixed sericite-argillic alteration can be seen (Fig. 3d). This study does not include mixed alteration types (propylite-argillic, sericite-argillic, etc.) since the purpose is a better understanding of the behaviour of chemical elements in distinct hydrothermal-metasomatic processes that form the main alteration zoning in the deposit.

A new alteration type was established during this study with leading mineral the Na mica – paragonite (Hikov, 2013). The quantity of paragonite varies from 13 to 36% in different samples. The mineral association includes kaolinite, sericite, quartz, pyrite, sometimes alunite, svanbergite, pyrophyllite and diaspore. This alteration type is relatively rare and occurs in depth in single samples from three drillholes in the SW part of the deposit. The paragonitic rocks look like the sericitic ones and it is difficult to discriminate them. In some cases sericite-paragonite mixture together with pyrite form over highly altered silicated rocks. Some features of mixed sericite-paragonite-advanced argillic alteration type are established also. Its place in the metasomatic zoning in Asarel deposit is still unclear.

The most intensive alteration which resulted from acid leaching of volcanic rocks is represented by the monoquartzite (silicic) rock. Ignatovski (1981) described two small lens-like bodies, 5–10 m thick, of monoquartzites among the alunite quartzites at the top of Razslatitsa peak.

Propylite altered rocks are widespread in the bottom levels and to the periphery of the deposit. There is a wide range of alteration degrees – from partial to whole replacement of the primary minerals. Propylitic association consists of chlorite, albite, epidote, sericite, carbonate, zeolites, pyrite, etc. (Fig. 3b, c).

Unaltered volcanic and intrusive rocks cannot be seen within and close to the deposit, so for the geochemical comparisons are selected samples from the least altered propylitic rocks. Comparatively fresh volcanic rocks are found ~2 km to the west (Fig. 3a).

It is not always possible to define the primary rocks

which were affected by hydrothermal alteration in Asarel deposit. This study shows that advanced argillic alteration affected mainly Late Cretaceous volcanic and porphyritic rocks which are widespread in the central and western part of the deposit. These rocks are discussed together because they have similar chemical composition and were affected by all previously described alteration types. The Paleozoic granitoid rocks which are more common in the northern and eastern parts are less altered. Propylitic, intermediate argillic and sericitic alteration types are documented. The geochemical changes during the alteration of Paleozoic granitoids are presented separately. It cannot be excluded that these older rocks were affected by advanced argillic alteration but there are no preserved primary textures which can help us to confirm this suggestion.

GEOCHEMISTRY OF HYDROTHERMALLY ALTERED LATE CRETACEOUS VOLCANIC AND PORPHYRITIC ROCKS

Geochemistry of major (petrogenic) elements

To estimate the “gains” and “losses” of the components during the hydrothermal alteration in Asarel deposit the method of Lindgren, which was popularized by Nakovnik (1958) was used. This method estimates the influence of the porosity of altered rocks by comparing the quantity of substances in equal volume. The altered rocks have wide variations in the volume density and in the porosity (Table 1). The argillic rocks have the lowest density (to 1.66 g/cm³) and the highest porosity (to 29.9%). The sericitic rocks also have high porosity. One representative sample from each alteration type was selected and the results should be considered as tentative and only directed to correct interpretation of chemical analyses. Concentration changes (“gain-loss” diagram) of major elements in the zones of hydrothermal alteration of volcanic and porphyritic rocks, normalized on unaltered rock composition are presented in Figure 4.

During the propylitic alteration there was an increase of Fe₂O₃, MgO, K₂O, loss of ignition (LOI) and decrease of CaO and Na₂O (Fig. 4). Weak-developed K-silicate alteration (K-feldspar-biotitic) is characterised by increasing of MgO and LOI and loss of Fe₂O₃, CaO, Na₂O, P₂O₅ and even of K₂O (-34%). Total depletion of all components except LOI is seen during argillic alteration, while SiO₂ and Al₂O₃ are less depleted. Sericitization is characterised by gain of LOI and loss of Fe₂O₃, MgO, CaO, Na₂O and P₂O₅. Actually, K₂O does not change as compared to unaltered rocks. During the paragonitic alteration Na₂O and K₂O are dissolved equally (~50%) but their quantities are enough to define the alteration. Pyrophyllitic alteration is characterised by gain of TiO₂, Al₂O₃, LOI, P₂O₅ and almost total loss of MgO, CaO, Na₂O and K₂O. During the alunite advanced argillic

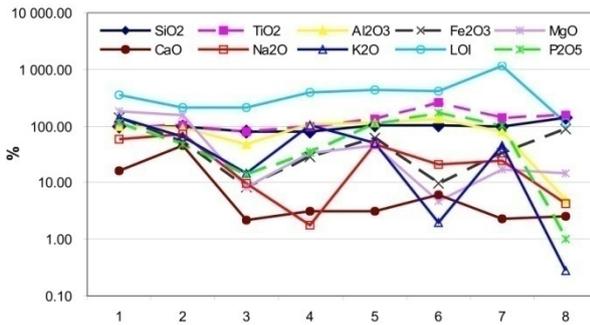


Fig. 4. Concentration changes (“gain-loss” diagram) of major elements in the zones of hydrothermal alteration of Asarel volcanic and porphyritic rocks, normalized on unaltered rock composition: 1 – propylitic; 2 – K-feldspar-biotitic; 3 – argillic; 4 – sericitic; 5 – paragonitic; 6 – pyrophyllitic; 7 – alunitic; 8 – silicic rocks.

alteration increasing of TiO_2 is seen, and especially of LOI (more than 10 times). Inert remain SiO_2 and P_2O_5 , while Al_2O_3 slightly decreases (~20%). All other components are depleted even K_2O and Na_2O which define the alteration type are depleted -55% and -75%, respectively. The strong silicic (monoquartzite) alteration is characterised by enrichment of SiO_2 and TiO_2 , inert behaviour of Fe_2O_3 and total depletion of all other components. Even Al_2O_3 is almost totally depleted (-95%).

Geochemical changes versus loss of ignition (LOI)

The loss of ignition (LOI) is determined by igniting of the weighted sample at 1050°C and can be considered as a monitor of alteration (Chambefort, 2005), because LOI is proportional mainly to H_2O^+ and CO_2 . Careful use of this monitor is needed because LOI depends not only on the degree of alteration but on the mineral composition – highest LOI content have alunitic altered rocks (rich of SO_4^{2-}), while monoquartzite rocks have low LOI. The presence of sulphide minerals (mainly pyrite) also influences the degree of LOI.

Mobility of some major and trace elements versus LOI (%) in altered volcanic and porphyritic rocks is presented in Fig. 5. Altered samples show significant variation of SiO_2 from 42.5 to 90 wt.% (Fig. 5a). MgO (Fig. 5b) and CaO are depleted from argillic, sericitic and especially from advanced argillic rocks. Similar is the behavior of Na_2O (Fig. 5c) which is partially enriched in alunitic alteration type. K_2O (Fig. 5d) concentrates in sericitic, argillic and partially in alunitic rocks.

Strontium (Fig. 5e) is depleted from propylitic, argillic and sericitic rocks and concentrates in advanced argillic rocks. Similar distribution but not as clearly expressed shows phosphorus. Rubidium (Fig. 5f) is depleted in the most of alteration zones but is accumulated only in sericitic rocks. The Ba contents are highly variable with maximal concentration in advanced argillic rocks. Lead has a trend to accumulate in advanced argillic alteration.

Characterization of inert (immobile) elements

Immobile elements are used for both classification of magmatic rocks and discrimination of hydrothermally altered and metamorphic rocks (Winchester, Floyd, 1977; Floyd, Winchester, 1978; MacLean, Kranidiotis, 1987). Elements such as Ti, Zr, Y, Nb, Ce, Ga, Sc, are considered to be immobile during the alteration processes.

Test for evaluation of immobility of the “classical” inert elements during the hydrothermal alteration in Asarel deposit has been done in this study. Ti and Zr (Fig. 5g, h) are comparatively inert during propylitization, argillization and sericitization (with slight decrease of Zr in propylitic and weak increase of Ti in sericitic rocks). Significant variations of concentrations of these elements are seen in advanced argillic rocks (both acid-sulphate and acid-chloride subtypes) but they are more inert compared to other elements. Close to them is V, which has positive correlation with Ti. The distribution of these inert elements in the alteration zones (Fig. 7c) confirms that their comparative immobility was influenced by highly intensive advanced argillic alteration. This influence is manifested by partial redistribution with slight increase of Ti and Zr and decrease of V. Ti and Zr have well expressed positive correlation in fresh and weakly altered rocks. This correlation disappears in advanced argillic zone, so it is unessential for all samples.

Distribution of elements in the zones of hydrothermal alteration

The distribution of trace elements in the alteration zones from fresh rocks to highly altered types is presented (Fig. 7) to elucidate the geochemistry of hydrothermal alteration in Asarel deposit. Some major elements which are important to the behaviour of trace elements are also discussed.

Calcium has high mobility during hydrothermal alterations (Fig. 7a). The quantity of CaO in altered rocks is very low (<0.2%). Only in propylitic rocks it is higher (mean 1.12%, sometimes up to 3–4%) because of the presence of carbonate minerals. **MgO** is absent from advanced argillic rocks (Fig. 7a). Its quantity in argillic and sericitic rocks is ~1%, while in propylitic rocks it increases up to 2.78% which is higher than in unaltered rocks. Chlorite as main mineral of magnesium was deposited several times during the evolution of hydrothermal system in Asarel deposit.

Na_2O (Fig. 7a) is depleted during advanced argillic alteration but it is partially accumulated in alunitic rocks (together with K_2O form alunite). Its concentration in argillic rocks (1.19%) is due to the presence of albite while in the paragonitic alteration type Na_2O gets up to 1.69%. The highest contents of Na_2O are in propylitic rocks as a result of intensive albitization.

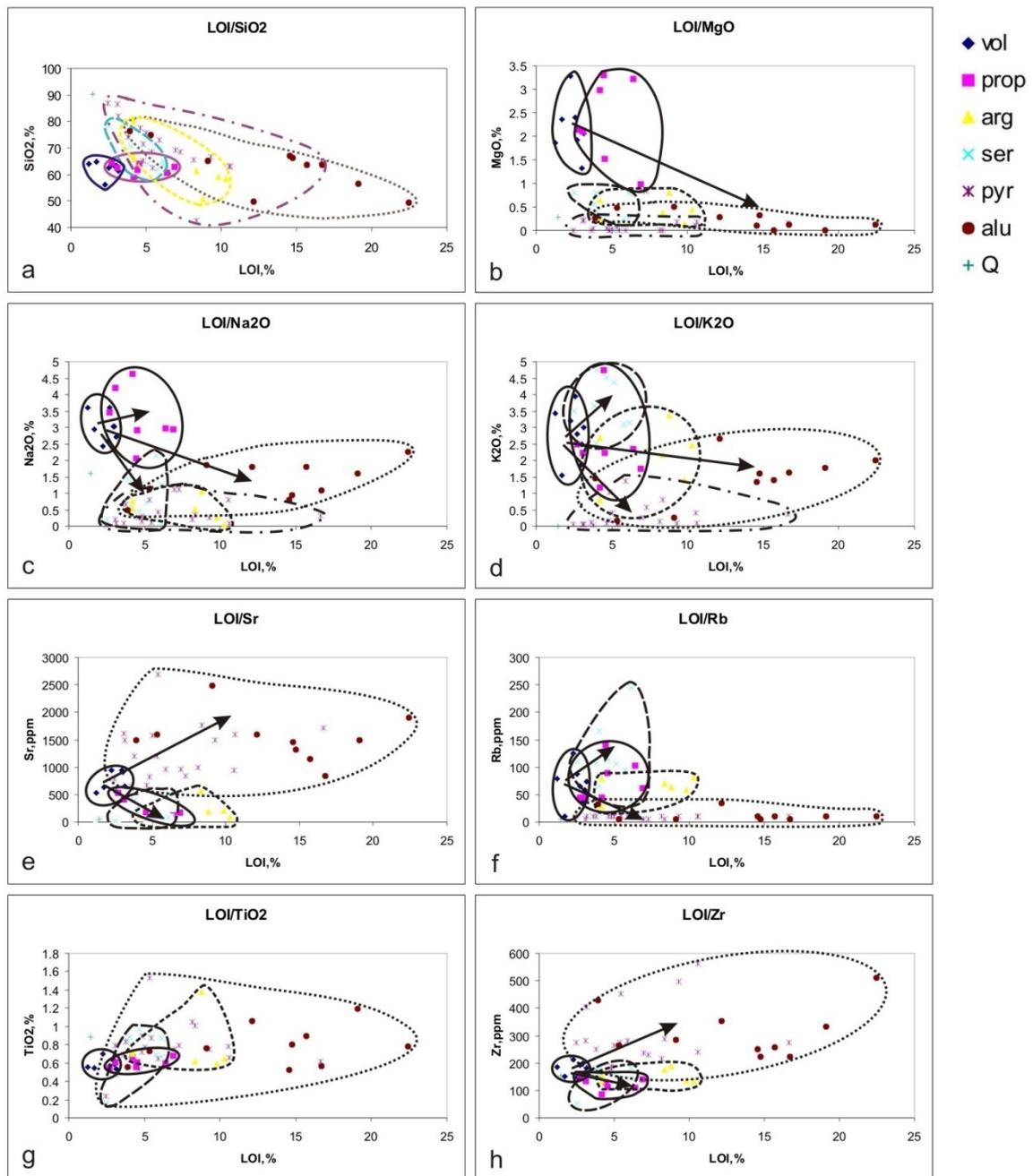


Fig. 5. Mobility of major and trace elements versus LOI (%) in altered volcanic and porphyritic rocks: *vol* – unaltered volcanic rocks, *prop* – propylitic, *arg* – argillic, *ser* – sericitic, *pyr* – pyrophyllitic, *alu* – alunitic, *Q* – monoquartzite (silic altered rocks).

K₂O is redistributed (Fig. 7a) but it has high contents in most of the altered rocks with maximum concentration of 3.60% in sericitic type. Propylitic and argillic rocks also contain significant amounts of K₂O due to the presence of sericite and K-feldspar. It is depleted from pyrophyllitic rocks while in alunitic rocks it reaches up to 1.08%.

Strontium and **rubidium** have the most characteristic behaviour among all studied trace elements (Fig. 6a, 7b). Concentration of Sr in the propylitic rocks is 211 ppm which is significantly lower

than in the parent rocks. Its behaviour depends on that of calcium – they both are depleted and become mobile during the alteration of plagioclase into albite. In argillic rocks concentration of Sr is close to that in propylitic rocks (235 ppm) while Ca is practically depleted. Still lower is Sr content in sericitic rocks (140 ppm). With increasing of sericitization dissolution of apatite starts which also contains some amounts of Sr.

High increasing of Sr concentration (mean 1560 ppm, often over 3000 ppm) is seen in the zones of advanced argillic alteration (secondary quartzites).

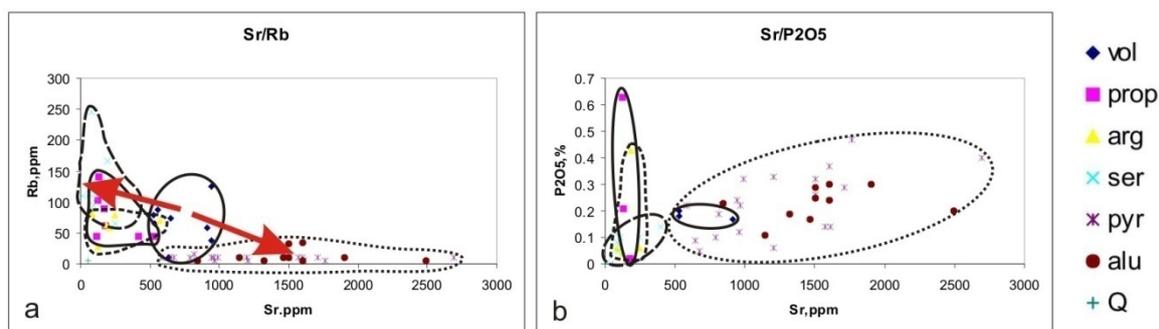


Fig. 6. Mobility of Rb (a) and P_2O_5 (b) versus Sr in altered volcanic and porphyritic rocks. Abbreviations are the same as in Fig. 5.

Strontium which is liberated from propylitic, argillic and sericitic rocks was introduced into the zones of advanced argillic alteration where it forms its own minerals phases. These are APS minerals, mainly svanbergite, woodhouseite and svanbergite-woodhouseite solid solutions (s.s.), as well as APS–alunite s.s. (Stoffregen, Alpers, 1987; Velinov et al., 1991; Hikov et al., 2010) which can explain the similar distribution of P and Sr in these altered rocks (Fig. 6b). Strontium contents are steadily high in all advanced argillic subtypes being slightly higher in alunite rocks (mean 1708 ppm).

Monoquartzites which are result of pervasive silification have very low Sr values of 51 ppm.

Rubidium has distribution that is opposite of that of Sr (Fig. 6a, 7b). Its concentration increases in K-bearing propylitic (92 ppm) and sericitic (119 ppm) rocks and decreases in intermediate argillic (75 ppm) and especially in advanced argillic (<16 ppm) rocks. Rubidium behaviour depends on that of potassium in the outer alteration zones but the relationship between these two elements disappears from alunitic alteration type where K_2O gets up to 1–2 %, while Rb is not registered. Rb is highly mobile during advanced argillic alteration and is moved out by the fluids. The Rb/Sr ratio is very characteristic and reflects described features of Rb and Sr behaviour. Rb/Sr ratio is 0.104 in volcanic rocks; it increases up to 0.458 in propylitic, and to 0.343 in argillic alteration, having highest values in the sericitic rocks – 0.890. Rb/Sr ratio strongly decreases in advanced argillic alteration and is 0.01.

Mean content of **Ba** slightly decreases with increasing the alteration degree (Fig. 7c). Its behaviour is comparatively inert being fully depleted only from monoquartzites. The Ba/Sr ratio varies from highest values in sericitic rocks (4.69) to lowest values in advanced argillic rocks (0.31). On the other hand, Ba concentrations have significant variations from 20 to 2000 ppm. The highest Ba content is related to barite mineralization and the presence of Ba as admixture in alunite and APS minerals (Hikov et al., 2010). There is a redistribution of Ba during advanced argillic alteration and deposition mainly in sulphate state.

The mean value of **Zr** (Fig. 7c) is constant in the different alteration zones. Its behaviour is defined as comparatively inert with slight enrichment in advanced argillic rocks. It is presumed that during advanced argillic alteration a partial or full dissolution of zircon occurred but Zr remains as a microscopic phase, probably of baddeleyite (see below).

Titanium and V have immobile behaviour (Fig. 7c) in spite of some variations of their contents in the different alteration types and in single samples as well. The differences are in slight trend to enrichment of Ti in advanced argillic alteration and in depletion of V from monoquartzites. Ti precipitates as the mineral rutile in more altered rocks. It is supposed that V is included as isomorphous admixture in rutile (Khashgerel et al., 2008; this study). There is a positive correlation between Ti and V in all alteration types.

The behaviour of **Mn** (Fig. 7d) is very similar to that of Mg – it is totally extracted from advanced argillic rocks and to a significant degree from argillic and sericitic rocks. The mean value of Mn in propylitic rocks (703 ppm) is the same as in unaltered volcanics (706 ppm) but its concentration varies from 40 to 2577 ppm. This possibly is a result of redistribution of Mn during later processes (ore deposition, supergene oxidation, etc.). **Lithium** (Fig. 7d) and **Cr** are very mobile during hydrothermal alteration and are fully depleted from all altered rocks.

HFS elements, such as **U**, **Th**, **Nb** and **Ta** have comparatively inert behaviour in the transitional zones of hydrothermal alteration and become partially mobile with the increasing of alteration degree in sericitic and especially in advanced argillic rocks (Fig. 7e). This is due to the relative stability of their minerals (e.g. zircon, titanium minerals, and apatite). To a certain extent, similar behaviours show **Ga** and **Sc** (Fig. 7f). They are weakly enriched in sericitic rocks and are impoverished in advanced argillic. More expressive depletion during advanced argillic alteration has **Y**, and especially **Cs** (Fig. 7f). Behaviour of **Cs** is very similar to that of Rb while **Y** is very close to HREE. Slight enrichment with the increasing of alteration degree with highest contents in alunitic rocks is seen for **Mo** and **Sn** (Fig. 7f),

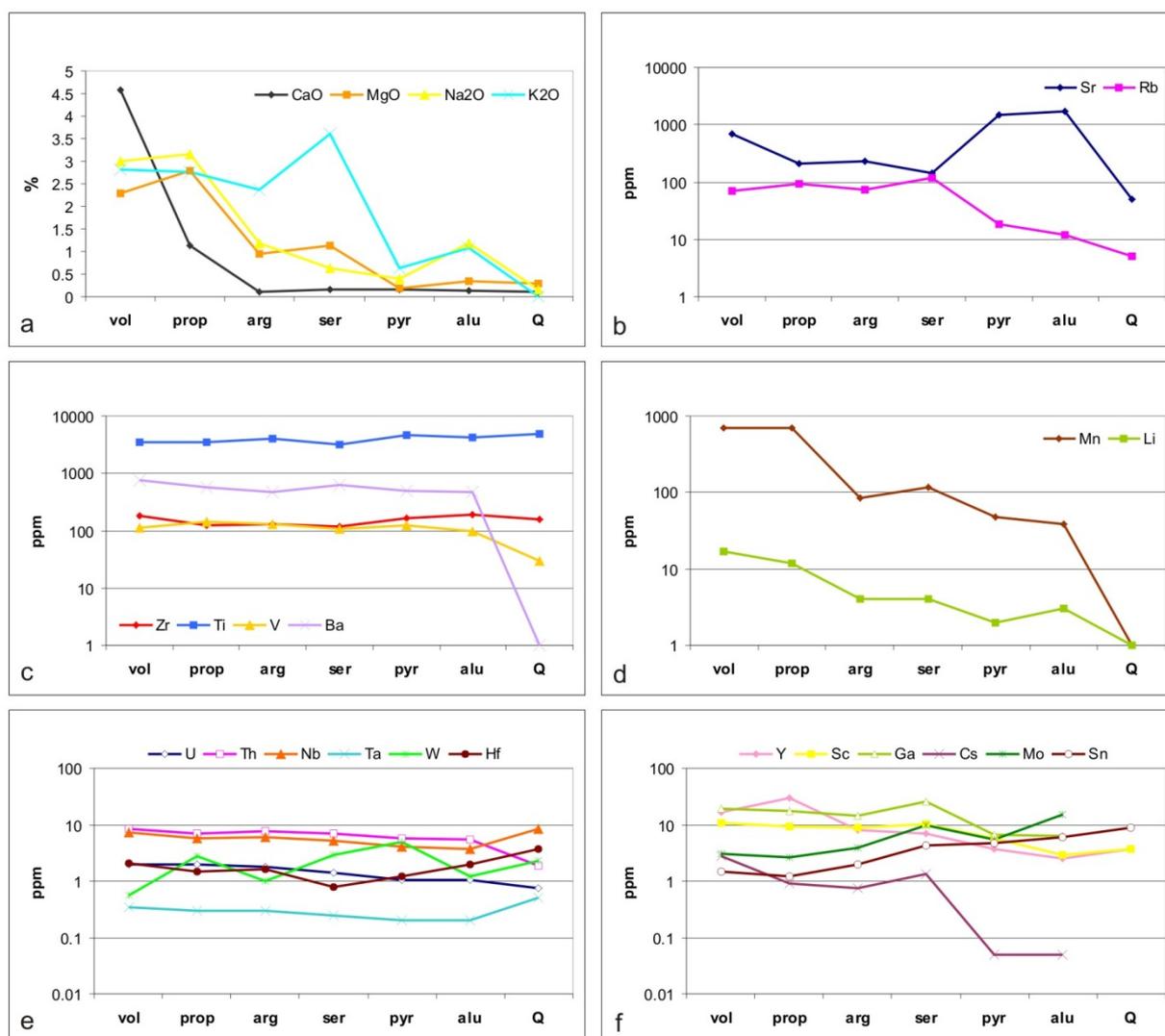


Fig. 7. Distribution of some major and trace elements in the zones of hydrothermal alteration of volcanic and porphyritic rocks from the Asarel deposit. Abbreviations are the same as in Fig. 5.

while **W** and **Hf** (Fig. 7e) have unsystematic distribution in the different alteration zones and their behaviour could be defined as comparatively inert.

Raised concentrations of **As** and **Sb** are registered in alunitic rocks. It is connected to high-sulphidation epithermal style (Petrunov et al., 1991; Strashimirov et al., 2002) in the upper levels of the Asarel porphyry copper system.

The distribution of base metals such as **Cu**, **Zn** and **Pb** in altered rocks is not discussed here because their behaviour depends on the ore-forming processes which postdate the formation of metasomatic rocks. Cu concentration gets up to 1–2% in the ore zones and falls down outside. All alteration types are affected by ore mineralization – mostly the sericitic, argillic and propylitic rocks, rarely advanced argillic ones. Supergenic processes have important role for redistribution and secondary concentration of Cu. Increased contents of Pb are documented in some

samples from alunitic rocks. Pb can be included in alunite (see below) and/or APS minerals, especially during the supergene stage since it is inert in sulphuric acid supergene conditions (Plant et al., 1988).

The evaluation of **Au** distribution in altered rocks from Asarel deposit is difficult due to the impossibility to analyse enough samples with one steady method. The different methods which were used have had important divergences of their limits of detection which makes comparison of data very difficult and sometimes even impossible. The results obtained in the Institute of Geochemistry (Irkutsk, Russia) have the highest precision with 2×10^{-8} (0.2 ppb) limit of detection but they are not enough to make valid conclusions for the Au distribution. The data (Table 1, 2) show Au enrichment in all alteration types which is highest in sericitic and pyrophyllitic rocks. The Au concentrations vary significantly from 1–4 ppb in the fresh rocks up to 300–400 ppb in some samples from altered rocks.

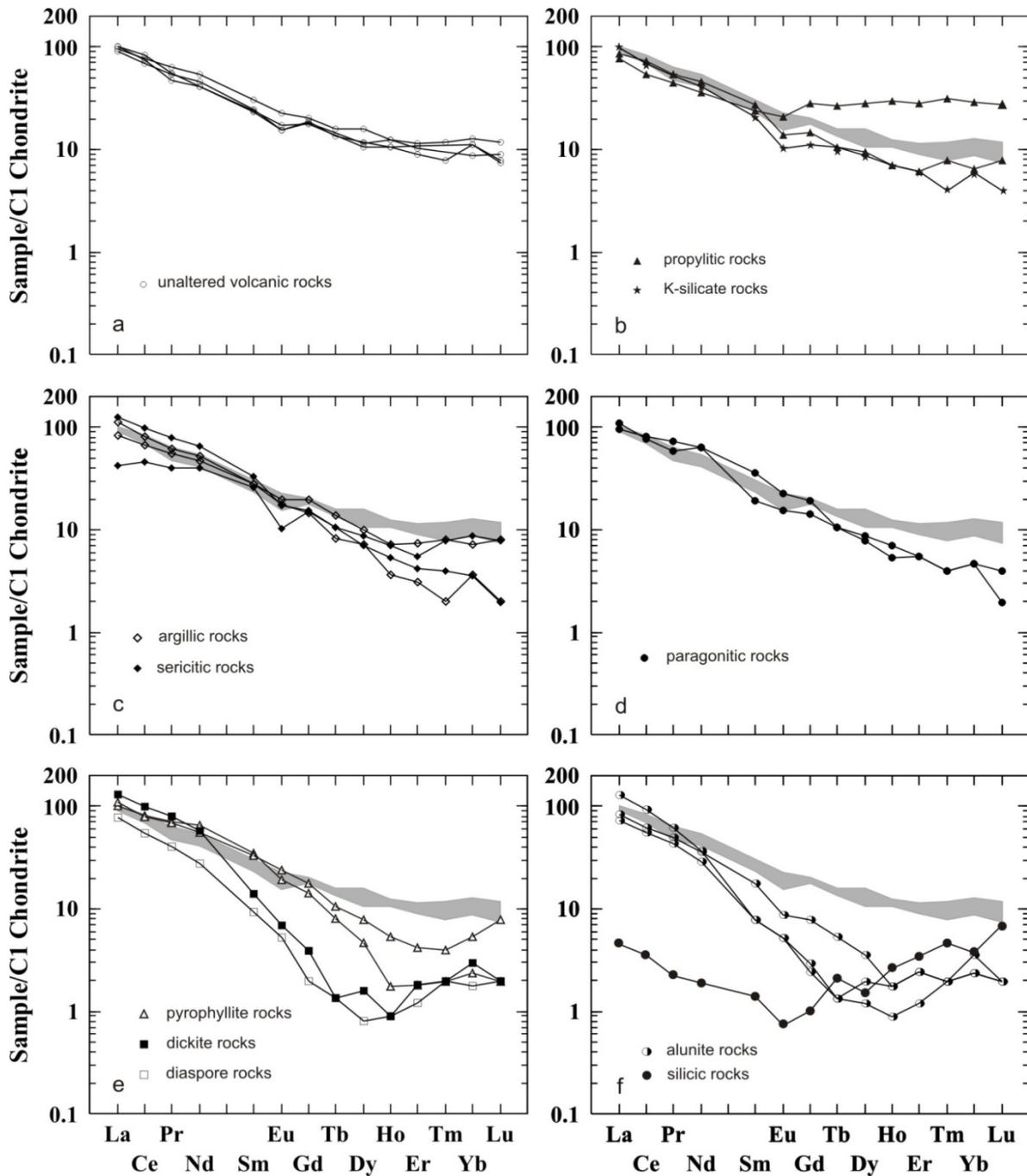


Fig. 8. Chondrite-normalized REE patterns of samples from fresh and altered volcanic and porphyritic rocks from Asarel porphyry copper deposit: *a* – unaltered rocks (shown as a grey field on *b*, *c*, *d*, *e*, *f*); *b* – propylitic and weak K-silicate altered rocks; *c* – intermediate argillic and sericitic altered rocks; *d* – paragonitic altered rocks; *e* – pyrophyllite, dickite and diasporite advanced argillic altered rocks; *f* – alunite and silicic advanced argillic altered rocks.

The most enriched sericitic rocks have significant variations in Au concentration, too. One can conclude that the host rocks were enriched in Au about five to ten times during the hydrothermal alteration but later there was additional gold deposition into the most appropriate environment, such as the sericitic and pyrophyllitic altered rocks. The preliminary data of Velinov et al. (1989)¹ show similar results: variable contents of Au in

single samples and concentration in sericitic and argillic rocks. The high values of Au are connected with pyrite and rarely chalcopyrite mineralization.

Limited data on Ag behaviour (Tables 1, 2) show that its values remain constant in all alteration zones. There is a slight enrichment in propylitic (0.26 ppm) and sericitic (0.31 ppm) rocks, as well as in monoquartzites (0.30 ppm).

Table 1
Selected chemical analyses of hydrothermally altered rocks from Asarel deposit

Sample Rocks	144 1	260 1	261 1	266 1	324B 2	58 3	786/103 3	86a 4	787/96 4	74a 5	783/39 5	791/58 6	274 7
SiO ₂ , %	63.97	64.7	56.01	62.54	64.72	61.8	63.89	79.26	59.18	63.65	64.6	67.23	68.57
TiO ₂	0.56	0.55	0.7		0.6	0.56	0.61	0.7	0.6	0.67	0.97	1.29	1.53
Al ₂ O ₃	15.96	15.21	18.27	16.08	15.63	15.94	18.92	11.89	25.99	22.17	19.95	18.44	22.39
Fe ₂ O ₃	4.69	5.03	6.76	4.93	2.49	6.17	4.38	0.6	2.02	1.59	4	2.81	0.46
MgO	1.86	2.37	3.29	2.4	3.15	3.31	1.52	0.25	0.14	0.78	0.32	0.83	0.09
CaO	4.23	5.37	6.49	3.87	2.01	0.7	0.39	0.15	0.07	0.17	0.14	0.13	0.27
Na ₂ O	3.61	2.95	2.44	2.58	2.73	2.07	2.91	0.55	0.04	0.09	0.47	1.69	0.11
K ₂ O	3.43	1.53	3.19	3.93	2.4	4.75	2.23	0.8	1.41	4.43	4.52	1.69	0.07
P ₂ O ₅	0.18		0.25		0.09	0.21	0.15	0.04	0.11	0.08	0.12	0.27	0.33
S	0.09		<0.04		0.1	2.58	0.12	0.01	0.99	<0.04	1.35	2.12	0.2
LOI	1.23	1.72	2.27	2.56	2.83	4.46	4.55	H ₂ O ⁺ -4	9.83	6.14	4.63	5.4	5.37
Ba, ppm	567	1099	977	671	212	1538	442	180	328	700	648	282	259
Zr	185	152	212	147	169	132	112	135	133	144	165	232	276
Sr	529	632	943	554	451	134	168	122	206	81	58	1029	1203
Rb	79	<20	125	87	98	141	89	27	58	245	114	45	1.3
Mn	768	828	1060	911	217	570	553	45	137	147	145	7	2
Cr	15	<10	<10	11	80	10	20	9	17	<10	10	9	2
V	79	101	153	123	81	94	130	81	135	147	165	121	222
Cu	28	40	56	24	700	2000	470	54	568	125	14	48.07	11
Zn	41	48	79	45	23	76	74	6	20	10	10	15.2	4
Pb	9	21	26	21	10	83	6	21	100	4	12	37.71	11
Ni	1	1	1	1	20	1	1	1	3	1	1	3.3	1
Co	6	11	14	9	8	19	8	1	7	3	10	8	1
Li	4	38	30	17	14	15	8	3	9	4	12	30.2	2
Ag	0.16		0.349		0.187	0.219	0.291	0.19	0.368	0.118	0.1	0.069	0.046
Au	0.0047	0.0042	<0.1	0.0015	0.0048	0.0027	<0.1	0.1	<0.1	0.0017	0.1	<0.1	0.004
Cl	310	310		310	480	210		210		210			240
F	1130	<100		<100	750	1250		760		1130			<100
Mo	5.91		0.32		19.32	4.4	0.98	4.62	3.09	15.48	3.83	25.21	3.86
W	0.4		0.7		0.5	5.1	0.5	0.9	1.1	4.3	1.5	5.3	0.8
Sn	1.6		1.3		0.9	1.1	1.3	2.3	1.7	2.1	6.4	7.4	8.2
Sc	7.2		13.9		13.4	7.3	11.6	6.2	11.2	9.6	10.7	10.4	9.5
Ga	17.33		20.9		16.33	17.18	17.52	9.58	19.5	26.04	24.63	7.62	6.38
Y	14.6	10	18.5	11	12.4	10.6	49.3	5.5	10.7	6.8	7.1	8.7	3.6
Hf	0.9		3.24		0.29	1.09	1.79	1.44	1.79	0.95	0.6	0.48	0.48
Ta	0.4		0.3		0.7	0.3	0.3	0.3	0.3	0.3	0.2	0.2	0.2
Nb	7.3		7.18		8.42	5.62	5.68	5.81	6.03	7	3.45	3.91	4.83
Cs	0.4		5.1		1.6	0.9	0.9	0.4	1.1	1.8	0.9	1.2	<0.1
U	2.2		1.7		2.6	1.5	2.4	1.8	1.8	1.7	1.1	0.8	1
Th	9.2		7.9		15.2	5.9	7.8	7.2	8.3	8.2	5.5	5.2	5.2
As	0.9		2.9		0.8	1.1	0.6	0.4	0.3	1.1	1.3	0.7	0.7
Sb	0.28		0.59		0.03	0.04	0.09	0.03	0.06	0.03	0.15	0.05	0.11
La	21.4	24	22.4	24	23.2	20.5	18	26	19.1	9.9	29.8	22.9	24.1
Ce	42.33	46	47.56	51	42.36	44.5	33.48	48.24	40.45	28.01	59.56	49.6	49.67
Pr	5.1	4.5	6	5.3	5	5.2	4.2	5.8	5.2	3.8	7.5	7	6.7
Nd	21.7	19	25.3	19	19.4	21.6	16.9	23.9	21.2	18.5	30.3	29.6	30.8
Sm	3.8	3.7	4.7	3.6	3.2	4.2	3.7	4.2	4.2	4	5	5.5	5.4
Eu	0.9	1	1.3	0.9	0.6	0.8	1.2	1	1.1	0.6	1	1.3	1.1
Gd	3.8	3.6	4.2	3.7	2.3	3	5.8	2.9	4	3.1	3.2	3.9	2.9
Tb	0.5		0.6		0.4	0.4	1	0.3	0.5	0.4	0.4	0.4	0.3
Dy	3	2.7	4	2.9	2.2	2.4	7.1	1.8	2.5	2.2	1.8	2	1.2
Ho	0.6	0.6	0.7	0.7	0.4	0.4	1.7	0.2	0.4	0.4	0.3	0.3	0.1
Er	1.5	1.8	1.9	1.7	1	1	4.7	0.5	1.2	0.9	0.7	0.9	0.3
Tm	0.2		0.3		0.1	0.2	0.8	<0.1	0.2	0.2	0.1	0.1	<0.1
Yb	1.9	1.9	2.2	1.5	1	1.1	4.9	0.6	1.2	1.5	0.6	0.8	0.4
Lu	0.2	0.19	0.3	0.23	0.1	0.2	0.7	<0.1	0.2	0.2	<0.1	<0.1	<0.1
∑ REE	106.93	108.99	121.46	114.53	101.26	105.5	104.18	115.44	101.45	63.81	140.26	123	122.97
La/Yb _{cn}	8.08	9.06	7.38	11.48	16.64	13.37	2.63	31.08	11.42	4.73	35.63	20.51	43.22
Eu/Eu _{cn} *	0.72	0.83	0.88	0.75	0.64	0.66	0.79	0.83	0.81	0.5	0.71	0.82	0.77
Rb/Sr	0.149	<0.02	0.133	0.157	0.217	1.052	0.53	0.221	0.282	3.025	1.966	0.044	0.001
dens.,g/cm ³	2.66	2.69			2.51	2.67	2.43	1.66	1.86	2.14	2.59	2.66	2.55

Table 1 (continued)

Sample	786/74	786/150	780/108	91	271a	784/118	785/48	788/117	271	80	234	75	310
Rocks	7	7	8	9	10	10	10	10	11	12	13	14	15
				86.58	66.15	49.75	49.21	63.57	90.31	66.48	66.57	82.01	79.77
SiO ₂ , %	75.71	64.97	63.36										
TiO ₂	0.77	0.62	0.66	0.79	0.8	1.06	0.78	0.9	0.88	0.37	0.53	0.07	0.08
Al ₂ O ₃	16.88	14.89	18.95	7.94	13.29	27.3	20.23	13.86	0.8	14.75	14.59	8.01	11.56
Fe ₂ O ₃	0.45	1.14	1.27	0.86	1.53	4.45	2.43	2.63	4.1	3.4	4.48	1.16	0.19
MgO	0.02	0.16	0.18	<0.02	<0.02	0.28	0.13	<0.02	0.28	2.31	2.93	0.35	0.22
CaO	0.23	0.3	0.47	0.08	0.1	0.15	0.09	0.23	0.11	3.46	0.53	0.07	0.04
Na ₂ O	0.07	0.32	0.1	0.06	1.17	1.8	2.27	1.79	0.16	2.56	2.03	0.18	0.13
K ₂ O	0.41	0.38	0.08	0.06	1.61	2.65	1.99	1.39	0.01	4.15	4.2	2.54	2.77
P ₂ O ₅	0.14	0.29	0.37	0.14	0.19	0.3	0.3	0.21	0.08	0.1	0.1	0.01	0.03
S	0.11	FeS ₂ 12.4	FeS ₂ -7.37	0.17	SO ₃ -11.4	4.90	SO ₃ -19.3	SO ₃ -12.9		0.15	0.94	0.1	0.04
LOI	5.03	H ₂ O-4.2	H ₂ O-6.4	3.08	14.73	12.13	22.45	15.72	1.43	1.97	3.46	1.78	1.73
Ba, ppm	241	865	318	102	504	2184	1526	385	26	873	600	196	544
Zr	265	274	562	280	222	354	510	257	154	108	137	62	58
Sr	1573	1709	2920	1612	1320	1600	2638	1143	51	261	144	9	12
Rb	9.3	<20	1.1	0.8	1	34	1.5	1.5	2	96.5	146.1	63.7	79.8
Mn	12	83	8	7	7	92	8	10	74	1218	1736	14	9
Cr	2	<10	7	4	11	14	14	5	31	35	69	5	3
V	170	114	93	46	45	149	94	99	29	74	87	69	20
Cu	4	271	11	23	18	496	39	44	29	59.92	120.22	328.63	52.28
Zn	2	7	2	5	1	4	2	6	3	53.5	358.3	5.8	3
Pb	32	84	23	61	29	68	117	31	5	12.18	65.86	4.93	1.27
Ni	2	<1	1	<1	2	1	1	1	<1	16.8	30.9	1.5	0.3
Co	1	11	12	1	2	11	1	1	<1	6.1	13.2	0.3	<0.2
Li	3	2	12	2	1	3	2	3	<1	7.5	14	3.1	3.6
Ag	0.192		0.149	0.122	0.165		0.17	0.161	0.3	0.06	0.366	0.986	0.043
Au	<0.1	0.4	0.0224	0.0027	<0.1	0.0144	<0.1	<0.1	<0.156	0.0197	<0.1	0.2	<0.1
Cl		280	1070	280		210				210			
F		480	120	940		640				940			
Mo	0.44		0.67	16.96	11.35		21.62	12.3	119*	0.33	0.84	8.3	0.88
W	2.9		13.5	2.9	1		0.9	1.7	2.3	1.6	0.8	0.4	1.8
Sn	1.7		4.7	4	4.4		10.7	3.3	8.7	2.6	8.2	3.3	1.4
Sc	9.8		2.6	1	2.5		2.9	3.3	3.61	6.6	9.7	2.1	1.1
Ga	11.97		7.16	1.51	3.45		6.19	9.21		15.66	15.53	8.33	5.61
Y	7.2		2.5	1.3	2.8		1.7	3.2	3.73	13.2	19.1	1.3	2.2
Hf	2.28		0.96	1.14	1.42		1.42	1.03	3.67	0.57	0.41	0.13	0.62
Ta	0.3		0.1	0.2	0.2		0.2	0.2	0.5	1	0.7	0.1	0.4
Nb	5.79		2.97	2.95	3.88		3.88	3.34	8.49	7.02	9.14	0.94	2.8
Cs	<0.1		<0.1	<0.1	<0.1		<0.1	<0.1	0.48*	0.7	2	0.6	0.3
U	1.9		0.6	0.8	1.1		1.1	1	0.76	6.2	4.9	0.2	0.5
Th	7.4		6.3	4.4	5.7		5.6	4.7	1.88	12	13.2	1.5	1.4
As	<0.2		2.6	1.7	19.5		13	60.7	6.25	0.8	2.3	1.2	0.2
Sb	0.31		0.16	0.12	0.32		0.44	0.5		0.17	0.07	0.35	0.11
La	26.1		30.8	18.4	17.1		30.9	19.9	1.08	13.8	23.7	1.5	7.7
Ce	48.79		59.66	32.65	33.92		56.75	37.94	2.2	26.88	43.47	3.12	12.89
Pr	6.6		7.5	3.8	4.1		5.9	4.7	0.21	3.1	5.5	0.3	1.6
Nd	25.9		27	12.7	13.4		17.4	17	0.89	11.6	20.8	1.4	5.4
Sm	5.1		2.1	1.4	1.2		1.2	2.7	<0.43	2.7	3.7	0.3	0.9
Eu	1.4		0.4	0.3	0.3		0.3	0.5	<0.084	0.7	0.8	<0.1	<0.1
Gd	3.6		0.8	0.4	0.5		0.6	1.6	<0.42	2.4	3.5	0.3	0.8
Tb	0.4		<0.1	<0.1	<0.1		<0.1	0.2	0.08	0.4	0.6	<0.1	<0.1
Dy	2		0.4	0.2	0.5		0.3	0.9	0.39	2.3	3.6	0.3	0.5
Ho	0.3		<0.1	<0.1	0.1		<0.1	0.1	0.15	0.5	0.7	<0.1	<0.1
Er	0.7		0.3	0.2	0.4		0.2	0.4	0.58	1.4	1.8	0.2	0.2
Tm	0.1		<0.1	<0.1	<0.1		<0.1	<0.1	0.12	0.2	0.3	<0.1	<0.1
Yb	0.9		0.5	0.3	0.6		0.4	0.4	0.64	1.8	2	0.1	0.3
Lu	0.2		<0.1	<0.1	<0.1		<0.1	<0.1	0.18	0.2	0.3	<0.1	<0.1
∑ REE	122.09		129.46	68.95	72.12		113.95	86.34	6.52	67.98	110.77	7.52	30.29
La/Yb _{cn}	20.8		44.18	43.99	20.44		55.41	35.68		5.5	8.5	10.76	18.41
Eu/Eu _{cn} *	0.95		0.78	0.93	1.01		0.96	0.68		0.82	0.67	0.5	0.18
Rb/Sr	0.006	<0.01	0.0004	0.0005	0.0007	0.02	0.0006	0.0013	0.039	0.37	1.01	7.08	6.65
dens., g/cm ³	2.47		2.73	2.57	2.55		2.61		2.57	2.6	2.65	2.26	2.64

Rocks: 1-11 – volcanic and porphyritic rocks: 1 – unaltered (144 – granodiorite porphyry; 260 – dacite; 261 – basaltic andesite; 266 – andesite); 2 – weak K-silicate altered granodiorite porphyry; 3 – propylitic; 4 – intermediate algallic; 5 – sericitic; 6 – paragonitic; 7 – pyrophyllitic; 8 – dickitic; 9 – diasporic; 10 – alunitic; 11 – silicic; 12-15 – granitoid rocks: 12 – unaltered; 13 – propylitic; 14 – intermediate algallic; 15 – sericitic; * probably raised value

Table 2
 Mean values of chemical elements in hydrothermally altered volcanic and porphyritic rocks from Asarel deposit

Alteration type	total samples	CaO %	MgO %	Na ₂ O %	K ₂ O %	Sr ppm	Rb ppm	Zr ppm	Ti ppm	Ba ppm	Mn ppm	Cr ppm	V ppm	Li ppm	total samples	Cu ppm	Zn ppm	Pb ppm
Unaltered rocks	7	4.58	2.29	2.99	2.82	684	69	181	3464	775	706	11	112	17	7	1014	57.1	15.3
Propylitic rocks	35	1.12	2.78	3.15	2.77	211	92	124	3518	584	703	~11	145	~12	11	1848	91.5	27.8
Argillic rocks	25	0.11	0.96	1.19	2.36	235	75	132	4016	475	86	~12	128	~4	15	429	10.5	49.7
Sericitic rocks	18	0.16	1.12	0.62	3.60	140	119	120	3255	616	116	~12	110	~4	12	236.2	7	19.2
Acid-chloride (pyrophyllite) subtype	45	0.17	~0.18	0.40	0.63	1468	18	168	4719	484	~47	~11	125	~2	22	152.3	5.5	45.6
Acid-sulphate (alunite) subtype	29	0.14	0.35	1.19	1.08	1708	12	192	4312	471	~39	~10	99	~3	10	87.2	4.8	60.8
Silicic rocks	1	0.11	0.28	0.16	0.01	51	2	154	4956	26	74	31	29	<1	1	29	3	5

Alteration type	total samples	U ppm	Th ppm	Nb ppm	Ta ppm	Y ppm	Sc ppm	Ga ppm	Cs ppm	Mo ppm	W ppm	Sn ppm	Hf ppm	As ppm	Sb ppm	total samples	Ag ppm	Au ppm
Unaltered rocks	2	1.95	8.55	7.24	0.35	16.55	10.55	19.11	2.75	3.11	0.55	1.45	2.07	1.9	0.43	3	0.21	0.0035
Propylitic rocks	2	1.95	6.85	5.65	0.3	29.95	9.45	17.35	0.9	2.69	2.8	1.2	1.44	0.85	0.065	5	0.26	0.0134
Argillic rocks	2	1.8	7.75	5.92	0.3	8.1	8.7	14.54	0.75	3.85	1	2	1.61	0.35	0.045	4(8)	0.23	0.0227
Sericitic rocks	2	1.4	6.85	5.22	0.25	6.95	10.15	25.33	1.35	9.65	2.9	4.25	0.77	1.2	0.09	8	0.31	0.0689
Acid-chloride (pyrophyllite) subtype	4	1.07	5.82	4.13	0.2	3.65	5.72	6.75	<0.1	5.48	5.02	4.65	1.21	1.27	0.17	13(10)	0.2	0.0539
Acid-sulphate (alunite) subtype	3	1.07	5.33	3.7	0.2	2.57	2.9	6.28	<0.1	15.09	1.2	6.13	1.93	31.07	0.42	5(4)	0.21	0.0173
Silicic rocks	1	0.76	1.88	8.49	0.5	3.73	3.61		0.48*	119*	2.3	8.7	3.67	6.25		1	0.3	<0.156

* probably raised value

Geochemistry of rare earth elements

REE concentration in the studied unaltered volcanic rocks from the Asarel magmatic center is about 110 ppm (Table 1). Chondrite-normalized REE patterns (Fig. 8a) in these rocks are characteristic for island-arc subduction-related magmas (Pearce, 1982) with enrichment of LREE in relation to HREE ($(La/Yb)_{cn}$ varies from 7.38 to 11.5) and comparatively flat HREE patterns ($(Gd/Yb)_{cn}$: 1.58–2). Typical of these patterns is the presence of weakly expressed negative Eu anomaly ($Eu^* = 0.72–0.88$; average 0.80) which was also registered by Daieva, Chipchakova (1997) in the rocks from the Medet-Asarel magmatic center. Similar chondrite-normalized REE patterns in unaltered volcanic rocks from the same region but without negative Eu^* were described by Kamenov et al. (2007), and Nedialkov et al. (2007).

REE concentration in propylitic, K-feldspar–biotitic (weakly developed K–silicate alteration type), intermediate argillic, sericitic and paragonitic altered rocks (Table 1) and their chondrite-normalized patterns (Fig. 8b, c, d) are similar to those in the fresh volcanic rocks. Visible mobility of REE, mainly of MREE and HREE is seen with the increasing of alteration degree, especially in argillic, sericitic and paragonitic alteration types. LREE concentrations do not show differences from parent rocks, which is due to the preservation of apatite as their main mineral. Weak mobility of LREE is visible only in sericitic alteration probably as a result of starting of the apatite dissolution. The results on K–silicate alteration are preliminary because we have not analyzed typical pervasive K–silicate alteration from depth.

Significant changes in the behaviour of REE are observed in advanced argillic alteration (acid-chloride and acid-sulphate subtypes). REE patterns in pyrophyllite altered rocks show MREE and HREE fractionation which is stronger in dickite- and diaspore-bearing rocks (Fig. 8e). The mobility of MREE and HREE is related to increased F^- ions activity and low pH of fluids (Fulignati et al., 1999), and their ability to form stable complexes under these conditions. Relative immobility (sometimes with slight addition) of the LREE is explained not only with the instability of their complexes, but also with the presence of APS minerals which contain some amounts of La, Ce and Nd (Hikov et al., 2010). The ability of LREE to be sorbed in kaolinite group minerals (Aja, 1998) can also explain the relative immobility of LREE in these altered types.

REE behaviour in alunitic advanced argillic rocks (Fig. 8f) is very similar as in the dickite- and diaspore-bearing altered types while the depletion of MREE and HREE is stronger than in the pyrophyllitic rocks. Relative stability of LREE is connected to the presence of alunite and the ability of entrance of these elements into the alunite lattice replacing potassium (Fulignati et al., 1999; Kikawada et al., 2004). APS minerals from the alunite zone also contain small amounts of LREE – usually low, up to 1%, but there are cases with high

LREE content (for example: La_2O_3 – 3.01 wt.% and Ce_2O_3 – 6.82 wt.%) (Hikov et al., 2010).

Silicic alteration type is characterized by strong depletion of all REE (Table 1; Fig. 8f). It can be explained by their extraction from altered rocks by the low-pH hydrothermal fluid and the lack of secondary minerals which can take them in their lattice.

Mobility of chemical elements according to multicomponent diagrams

Multicomponent diagrams (spidergrams) allow us to make more complete evaluation of the mobility of chemical elements during the hydrothermal alteration.

Multicomponent diagrams (Fig. 9a) of fresh rocks (granodiorite porphyry (144) and high-K basaltic andesite (261)) are similar, the difference being that volcanic rocks are enriched in Cs and Ba and reduced in Pb, and are characterized by enrichment of LILE and depletion of HFSE which is typical of island-arc subduction-related magmas (Pearce, 1982), as well as Nb-Ta negative anomaly (Thompson et al., 1984). There are also minima of P and Ti, a maximum of Pb, especially for granodiorite porphyry, and comparatively high levels of enrichment of Sr that were registered for the part of rocks in the region by Kamenov et al. (2007).

Spidergrams of propylitic and weakly altered K–silicate types are similar to unaltered rocks, only depletion of Sr from propylitic rocks and low mobility of Ba, P, Y, and HREE are visible (Fig. 9a). Argillic rocks are characterized by depletion of LILE (Cs, Rb, Ba, K, Sr), P, Y, HREE, and enrichment of Pb, while in sericitic rocks Cs, Rb, Ba, K concentrate (or are immobile), and Pb, Sr, P, Y, and HREE are strongly depleted (Fig. 9b). HFSE (Th, U, Nb, and Ta), Ti and partially LREE are comparatively inert in both argillic and sericitic alteration types. Depletion of LILE, HFSE, Y, and HREE is registered for paragonitic alteration, while other elements are comparatively inert (Fig. 9b).

Acid-chloride subtype advanced argillic alteration is characterized by depletion of the most elements which is better expressed for dickite and diaspore rocks in comparison to the pyrophyllite rocks (Fig. 9c). Highly mobile are Cs, Rb, K, Y, and HREE, while Ba, U, Nb, Ta and MREE are less mobile. Comparatively inert are Th, LREE, Zr, and Ti. Enrichment is visible only for Sr, sometimes for Pb, P and Zr.

Depletion of the most elements is also seen in the alunitic rocks (Fig. 9d). It is best visible for Cs, Rb, Y, and HREE, and in lesser extent for Th, U, K, Nb, Ta, and MREE. Inert behaviour have Ba, LREE (La, Ce, Pr, Nd), P, Zr and Ti. Enrichment is characteristic of Sr and Pb, as well as for Ba and Zr in some samples. Strong depletion of the most elements is seen for mono-quartzites: only Nb, Ta, Zr, and Ti are immobile.

Multicomponent diagrams as a whole confirm the previously made conclusions for the behaviour of trace elements during hydrothermal alteration. Only the gains of Pb in advanced argillic rocks are more visible here.

GEOCHEMICAL FEATURES OF HYDROTHERMALLY ALTERED PALEOZOIC GRANITOID ROCKS

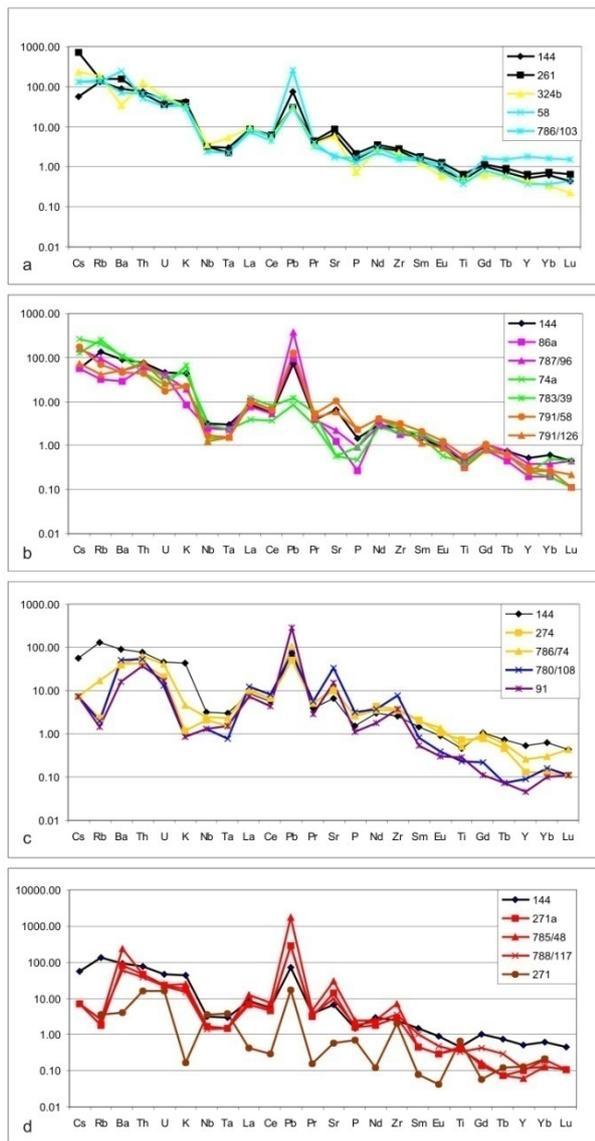


Fig. 9. Multicomponent diagrams of fresh and altered volcanic and porphyritic rocks from Asarel deposit, normalization on NMORB (Sun, McDonough, 1989): *a* – unaltered (144, 261), weak K-silicate altered (324b) and propylitic (58, 786/103) rocks; *b* – argillic (86a, 787/96), sericitic (74a, 783/39) and paragonitic (791/58, 791/126) rocks; *c* – pyrophyllite (274, 786/74), dickite (780/108) and diaspore (91) rocks; *d* – alunite (271a, 785/48, 788/117) and silicic (271) rocks.

On the other hand, these diagrams give a possibility to evaluate the different degree of mobility of each element.

The NE part of the Asarel deposit is built up of Paleozoic granitoid rocks from the Smilovene pluton (Katzkov, Iliev, 1993; Nedialkov et al., 2007). According to Popov et al. (2012) these rocks from the basement were lifted and now are at the same altitudinal level with the advanced argillic altered volcanics. This probably is the main reason why the hydrothermal alterations partially affected Paleozoic granitoides. Only propylitic, intermediate argillic and sericitic alteration types are established.

The data on chemical composition of altered granitic rocks from the region of Asarel deposit are very limited (Table 1). They are used to describe the behaviour of the elements in the metasomatic processes but can only be considered as preliminary.

The following changes of the major elements are registered: enrichment of TiO_2 , Fe_2O_3 , MgO and LOI , inert behaviour of SiO_2 , Al_2O_3 , K_2O , and decreasing of CaO and lesser of Na_2O during propylitization. Argillic and sericitic granites have similar “gain-loss” picture – depletion of all components except SiO_2 which is enriched. The depletion in argillic rocks is stronger which is connected to their lower density. K_2O concentrates in sericitic rock with respect to argillic ones but its content is lower than in unaltered granitoides.

Distribution of trace elements in the alteration zones is presented in Fig. 10. Strontium is partially depleted from propylitic and almost totally from argillic and sericitic altered granitoides (Fig. 10a). Strontium behaviour is the same as in the same type of altered volcanic rocks. Similar behaviour but with slight enrichment in propylitic rocks have Y and Cr (Fig. 10a). Comparatively inert during hydrothermal alterations are V, Ba, Zr, and Ga (Fig. 10b) but each element decreases in a certain zone (V – in sericitic; Ba – in argillic; Zr and Ga – in argillic and sericitic). A group of elements (Hf, Ta, Nb, U, and Th) remains inert during propylitization but is fully depleted during argilization and partially during sericitization (Fig. 10c).

Other group (Rb, Cs, Li, and Sc) is enriched in the propylitic rocks. The concentrations of these elements in argillic and sericitic rocks are the same as or slightly decreased than in the fresh rocks (Fig. 10d). It can be concluded with some approximation that these elements follow K behaviour during alteration. Ore elements are divided into two groups. Copper, Ag and Mo are enriched in propylitic and especially in argillic rocks, W – in sericitic, and Sn – in propylitic (Fig. 10e). These

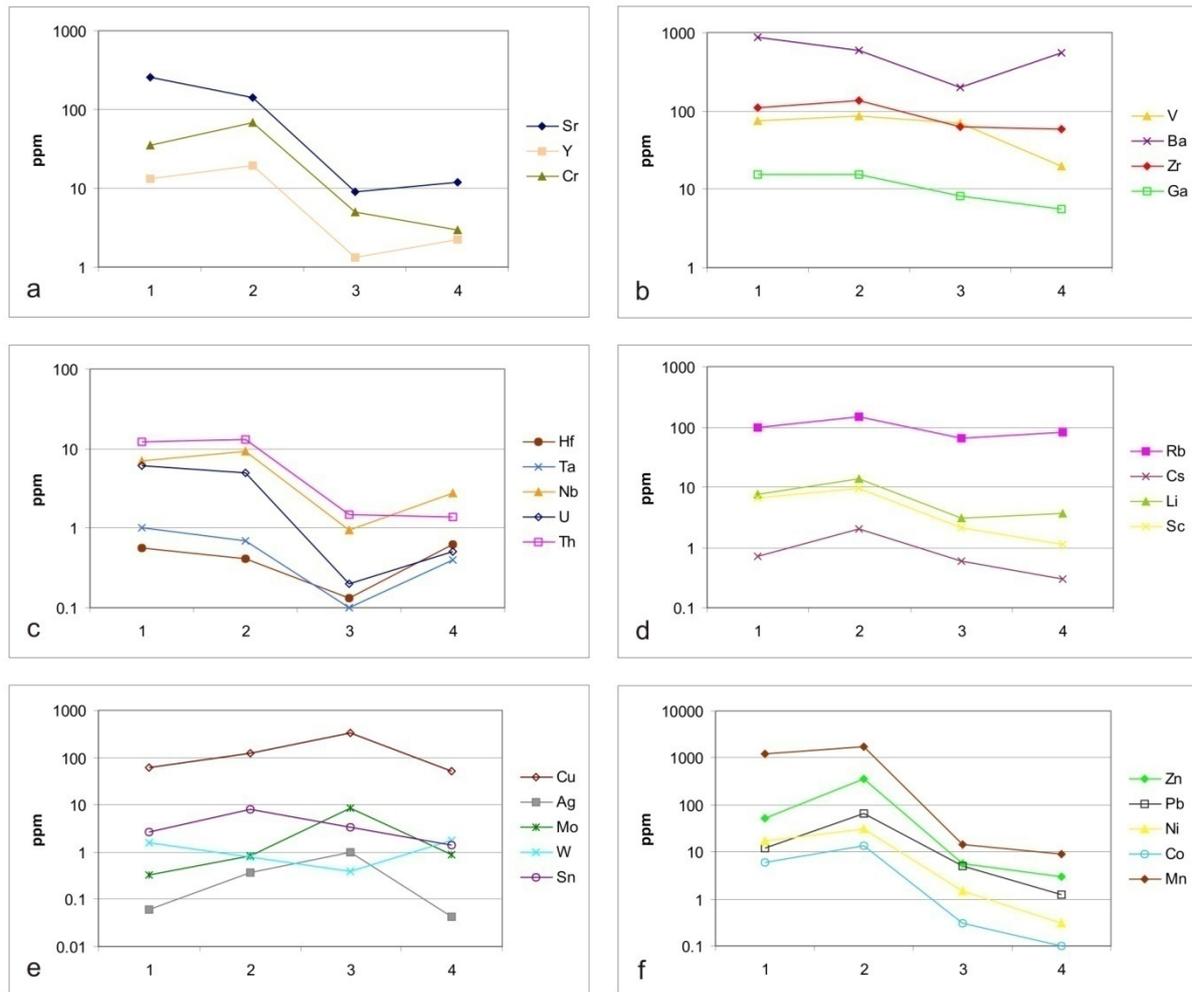


Fig. 10. Distribution of trace elements in the zones of hydrothermal alteration of Paleozoic granitoid rocks from the Asarel deposit: 1 – unaltered rocks; 2 – propylitic; 3 – argillic; 4 – sericitic rocks.

ore elements show no significant loss in any zone. The second group (Zn, Pb, Ni, Co, Mn) increases in propylitic rocks, while it is almost depleted from argillic and sericitic types (Fig. 10f). Probably there was a redistribution of these elements during hydrothermal alteration with migration to the periphery of the deposit into the propylitic rocks where the deposition as vein mineralizations is possible (Bogdanov, 1987; Sillitoe, 2010).

Geochemical analysis of granitic rocks from the Asarel porphyry copper deposit indicates that REE are mobile during different hydrothermal alteration processes. Investigations of the mobility of these elements in granites (Alderton et al., 1980; Baker, 1985) showed not always identical REE behaviour. The survey of Yongliang, Yusheng (1991) confirms the lack of systematic changes in the behaviour of both the REE and the value of Eu^* during hydrothermal alteration of granitic rocks.

Chondrite-normalized REE pattern in the fresh granite (Fig. 11) is characterized by slight enrichment of LREE with respect to HREE ($(La/Yb)_{cn} = 5.5$) and

moderate negative Eu^* (0.82). Weak enrichment of all REE with increasing $(La/Yb)_{cn}$ ratio (8.5) and negative Eu^* (0.67) is more pronounced in propylitic altered granite. Two samples from fresh and propylitic granite have similar mineral composition, so it may be supposed that the higher ΣREE and Eu^* values result from higher concentration of apatite in the propylitic altered granite.

Depletion of all REE and predominance of LREE over HREE ($(La/Yb)_{cn} = 18.41$), accompanied by increasing negative Eu^* (0.18) are registered in the sericitic altered granite (Fig. 11d). During sericitization, REE which are liberated from the feldspars, are included into newly formed sericite. Only Eu has anomalous behaviour – it is evident that this element is probably in 2-valent form despite of oxidizing conditions and cannot be included in the sericite lattice. Similar REE behaviour was described for the sericitization of the Dartmoor granite (Ward et al., 1992).

REE pattern in the intermediate argillic altered granite (Fig. 11c) shows strong depletion of all REE and fractionation of the HREE with respect to the LREE

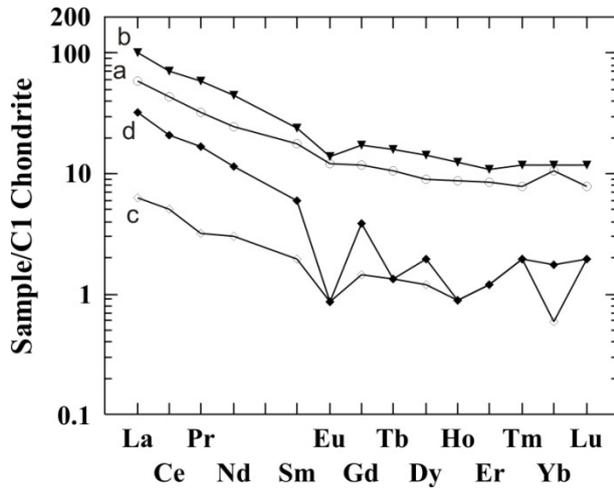


Fig. 11. Chondrite-normalized REE patterns of samples from fresh and altered Paleozoic granitoid rocks from Asarel deposit: *a* – unaltered rocks; *b* – propylitic rocks; *c* – argillic rocks; *d* – sericitic rocks.

$(La/Yb)_{cn} = 10.76$). Probably this is due to the prolonged weathering of this sample which has relatively higher porosity (10.2 %). The negative Eu^* also decreases ($Eu^* = 0.5$).

GEOCHEMISTRY OF ALUNITE GROUP MINERALS

The chemistry of the alteration minerals is of great importance for studying the hydrothermal-metasomatic processes. Some of them do not have significant diversity in their composition, e.g. pyrophyllite, kaolinite, dickite, diaspore, and zunyite. Others, however, such as alunite and APS minerals show considerable variations in their composition due to the different physical and chemical conditions of their formation and could be used as indicative minerals for the geological environment (Sillitoe, Hedenquist, 2003). Finally, they can give answers to many questions about the geochemistry of some trace elements in the alteration zones.

The alunite supergroup (Jambor, 1999) consists of three mineral groups with more than 40 mineral species. The generalized formula of the group is $DG_3(TO_4)_2(OH,H_2O)_6$, where *D* are large cations (K, Na, Ag, H₃O, Ca, Sr, Ba, Pb, Bi, La, Ce, Nd) with coordination number larger or equal to 9. *G* site is occupied by cations in octahedral coordination (Al, Fe, Cu, Zn), and *T* site – by S, P and As in tetrahedral coordination. As a rule, if *D* position is occupied by 2-valent cations there are one phosphate and one sulphate anion in *T* site which leads to formation of great diversity of aluminium phosphate-sulphate (APS) minerals (Stoffregen, Alpers, 1987).

Alunite is the main mineral in the acid-sulphate advanced argillic alteration and is widespread in SW upper part of the deposit (Radonova, Stefanov, 1974; Ignatovski, Tzvetanov, 1981; Hikov et al., 2010). The alunite content is variable, from 10 to 60%. The mineral typically associates with quartz, APS minerals, rutile and pyrite, often with diaspore, dickite, kaolinite, pyrophyllite, zunyite and barite.

First data on APS minerals in Asarel were given by Velinov et al. (1989)¹ and Velinov et al. (1991) but their geochemical features are discussed in detail by Hikov et al. (2010). APS minerals are representative of advanced argillic alteration and can not be seen in less altered volcanic rocks. They usually occur as cores in the central part of alunite crystals and have pseudocubic or irregular form. Chemical zoning marking the transition alunite-APS minerals is often observed as APS minerals with complicated zoning due to the varying concentrations of K, Na, Ca, Sr, Ba, and/or REE. APS minerals also occur outside the alunitic zone in the pyrophyllite type advanced argillic alteration in association with quartz, pyrophyllite, dickite, kaolinite, diaspore, zunyite, pyrite ± alunite. APS minerals always occur but in trace amounts (1–2%) and for that reason their detection is difficult.

Alunites from Asarel are K-Na to natroalunites with Na/K ratio varying from 1:10 to 10:1 (Fig. 12a). Small admixtures of Ca, Sr and Ba, up to 0.10 *a.p.f.u.*, are permanent (Fig. 12a), while LREE, Fe, F, and As occur rarely. The increasing of 2- and 3-valent cations in *D* position is accompanying by increasing of PO_4^{3-} up to 0.12 *a.p.f.u.* Locally, Sr, Ca and Ba content increases (together up to 0.45 *a.p.f.u.*), as well as that of PO_4^{3-} up to 0.42 *a.p.f.u.* These are mixed alunite-APS phases (Fig. 12a).

APS minerals themselves are mainly svanbergite and woodhouseite-svanbergite s.s., rarely woodhouseite (Fig. 12b). Calcium/Strontium ratio varies from 10:1 to 1:19, being mostly between 1:1 and 1:10. Maximal concentration of Sr is 0.78 *a.p.f.u.* (SrO – 18.55 wt.%) which is close to pure svanbergite. Barium admixtures are permanent in low concentrations (0.01–0.1 *a.p.f.u.*) but there are some cases with high Ba content in mixed Ca-Sr-Ba APS s.s. (Fig. 12b) where Ba reaches up to 0.36 *a.p.f.u.* (BaO – 11.68 wt.%). LREE content (Fig. 12c) is usually low, ca. 0.03 *a.p.f.u.*, only sometimes it is higher (e.g. La – 0.08 and Ce – 0.19 *a.p.f.u.*). These are PO_4^{3-} -rich phases of florencite-svanbergite s.s.

PRELIMINARY LA-ICP-MS DATA ON THE GEOCHEMISTRY OF IMMOBILE ELEMENTS IN THE MONOQUARTZITES (SILICIC ROCKS)

Whole rock and mineral LA-ICP-MS analyses have been made for monoquartz (silicic) rocks which show that despite of the complete leaching of most components, some elements have inert behavior. They are connected with the following minerals:

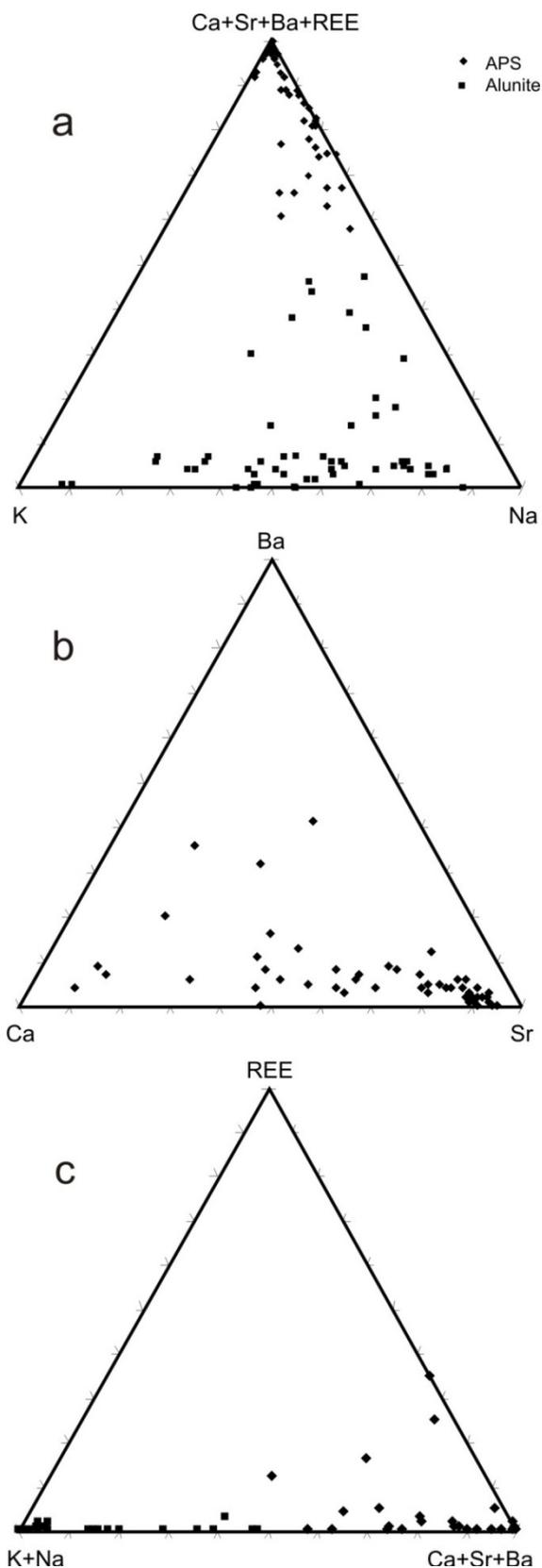


Fig. 12. *D* position diagrams of alunite and APS minerals (after Hikov et al., 2010)
a – K–Na–(Ca+Sr+Ba+REE);
b – Ca–Sr–Ba; *c* – (K+Na)–(Ca+Sr+Ba)–REE

Alunite. It is very rare and fine-grained, usually in small cavities. Besides K and Na, alunites contain admixtures of Sr (3873 ppm), Ba (1336 ppm), La (43 ppm), Ce (87 ppm), Pb (562 ppm), rarely Ti (~700 ppm), V (~100 ppm), Ga (~50 ppm), etc. The elements Sr, Ba, La, Ce, Pb are characteristic admixtures in alunite and in advanced argillic alteration as a whole but they are absent from monoquartzites. The very small quantity of alunite concentrates remnants of these elements. The presence of Pb is an important result because this element is difficult to measure by microprobe analyses. The second group (Ti, V, and Ga) has not been registered by all analysis. These are typical inert elements – Ti and V are mainly present in rutile, while for Ga there are no data on inclusion in other mineral.

Rutile. It can be seen as small crystals. Rutile is a typical product of advanced argillic alteration and is the main mineral form of Ti, which is inert and preserves even in monoquartzites. The following admixtures in rutile are registered with LA–ICP–MS (mean values): V (2116 ppm), Zr (2780 ppm), Nb (1264 ppm), Sn (1100 ppm), Hf (87 ppm), Ta (54 ppm), W (146 ppm), Th (~26 ppm), U (~20 ppm), rarely Y (~40 ppm), Mo (~130 ppm), sometimes HREE. These results show that rutile contains up to 100% of Sn, Nb and Ta, from 50 to 70% of V and W, about 20% of Th and U. The concentration of Zr varies significantly from 521 to 12 289 ppm. This is due to the presence of inclusions of zirconium phase in some rutile crystals which are registered during the analyses. Probably these inclusions are smaller than 5 μm . Thus, rutile contains from 5 to 50–60% of Zr according to the presence/absence of some inclusions. Till now this Zr phase was unknown despite that its existence independently out of rutile crystals has been registered during the whole rock analysis. It contains Zr, Hf, Y, REE (mainly middle and heavy), Th and U (qualitative analysis). It is possible that these are fine residua of dissolved zircon crystals, or fine-grained ZrO_2 , the mineral **baddleyite** which hosts the liberated Zr and its accompanying elements after zircon dissolution. In both cases there is partial or full zircon dissolution. Zr and Hf are immobile in such environment while the other elements are considerably depleted from monoquartz rocks, thus the formation of ZrO_2 is most likely.

Iron oxides and hydroxides. They have not been studied in detail. Preliminary data show that they can accumulate Mo, possibly Th, U, etc.

STABLE ISOTOPE GEOCHEMISTRY

Two samples of alunite rocks have been studied for stable isotopes of S, O and H (Hikov et al., 2010). The high values of $\delta^{34}\text{S}_{\text{SO}_4}$ define alunites from Asarel as magmatic–hydrothermal (Rye et al., 1992). From the coexisting alunite-pyrite pair is calculated temperature of formation of 290–295°C (Rye et al., 1992) which is consistent with the temperature deduced from the

mineral assemblage of alunite, diaspore, zunyite, pyrophyllite (~300°C) (Lerouge et al., 2006). Oxygen and H isotopes show domination of magmatic fluids, although with significant influence of meteoric waters (up to 50%). The calculated from S and O isotopes H₂S/SO₄ ratio is about 3–4 which also presumes domination of magmatic fluids (Ohmoto, Rye, 1979).

DISCUSSION

The deposition of porphyry copper mineralization in Asarel deposit is accompanied by the development of intensive hydrothermal alteration of propylitic, intermediate argillic, sericitic and advanced argillic types. Advanced argillic alteration resulted from the action of extremely acid (pH <2), rich of volatiles (CO₃²⁻, F⁻, Cl⁻, SO₄²⁻) magmatic-hydrothermal fluids mostly between 200 and 300°C (Meyer, Hemley, 1967; Hemley et al., 1980; Velinov et al., 2007; Hikov et al., 2010). During hydrothermal alteration significant to complete changes of mineral and chemical composition of the parent rocks took place (mainly of volcanic, in lesser degree of intrusive and metamorphic rocks) which erases the most of their initial characteristic (textural, mineralogical, petrological and chemical). It is very difficult and often impossible to identify the primary rock which was affected by advanced argillic alteration (sometimes by sericitization). Multiple hydrothermal events, tectonic processes, telescoping, ore deposition and supergene alteration additionally complicate the effects of hydrothermal alterations.

The alteration is so intensive that even inert elements such as Ti and Zr become partly mobile during advanced argillic alteration. Both elements are immobile in outer alteration zones and have positive correlation. Significant variations of Ti and Zr concentration are established in advanced argillic altered rocks, as well as lack of their positive correlation. These variations are not connected with “gains” or “losses” of the elements because their mean values remain invariable in the alteration zones (Fig. 7c). During advanced argillic alteration the main Ti and Zr minerals from magmatic rocks, titanite and zircon, respectively, are dissolved. The liberated elements form new mineral phases at once or after migration at a short distance in the same alteration zone. Titanium forms rutile which is very stable in highly acid conditions and preserves even in the most altered monoquartzites. The occurrence of Zr in these zones is unknown with certainty till now, while different models are possible: as admixture in clay minerals and diaspore (Gavrilenko, Sahonenok, 1986), alunite (Kashkai, 1970), rutile or unknown fine-grained zirconium phase, possibly ZrO₂. The present study of rutile with LA-ICP-MS shows that the most of Zr occurs as admixture in rutile and as fine-grained ZrO₂. Vanadium has similar low mobility during advanced argillic alteration and has significant positive correlation with Ti. Most probably V is included as isomorphous

admixture in rutile (Khashgerel et al., 2008) which was demonstrated with LA-ICP-MS in this study. Rutile also hosts Sn, W, Nb, Ta, Hf, partially U and Th which are comparatively inert in these conditions.

The other trace elements are highly mobile and are moved out from the fluids or are redistributed. The most characteristic and of great importance is the behaviour of Sr. The element is depleted from outer alteration zones and is accumulated in inner zones of advanced argillic alteration. This is interpreted as destruction of Sr-containing minerals during propylitization, argillization and sericitization and migration of Sr in the solutions probably as halogenic complexes (Burkov, Podporina, 1962) in sulphate-chloride hydrothermal fluids (Pampura, 1985) without being included in new minerals. The fluids become more acid and sulphate-bearing during advanced argillic alteration and optimum conditions for deposition of Sr²⁺ in its own minerals are created. APS minerals form in a broad interval of pH (3–8) and high activity of PO₄³⁻ (Stoffregen, Alpers, 1987; Ripp et al., 1998; Schwab et al., 2005). The presence of phosphate anion PO₄³⁻ (after apatite dissolution) is crucially important. Apatite fully preserves in propylitic and argillic altered rocks and dissolves partially in sericitic and completely in advanced argillic rocks in low pH acid environment (Stoffregen, Alpers, 1987). The liberated PO₄³⁻ and Ca²⁺ do not move out with the solutions but together with added Sr²⁺ and SO₄²⁻ from fluids form new aluminium phosphate-sulphate (APS) minerals. At some places Ba also occurs which locally has high concentrations and is registered in APS minerals. According to Stoffregen, Alpers (1987) APS minerals can coexist with alunite and kaolinite at 250°C. Muscovite is in equilibrium with both APS minerals and apatite which can explain the presence or absence of apatite in sericitic rocks. Apatite does not coexist with alunite and kaolinite, so small quantities of APS minerals are to be found at advanced argillic altered rocks, under conditions that PO₄³⁻ does not move out with the fluids. For the presence of APS minerals and high Sr concentration in pyrophyllitic advanced argillic rocks similar arguments apply at somewhat higher temperatures – between 270 and 350°C. Part of Sr is included also in alunite and alunite-APS s.s. (Kashkai, 1970; Hikov, 2004a; Hikov et al., 2010; Chang et al., 2011; Georgieva, Velinova, 2012a).

All geochemical data suggest that Sr is not added with hydrothermal fluids from depth and its high concentrations are result of mobilization and redistribution during alteration because the volume of the Sr-leached external zones exceeds several times the volume of the enriched zones. Similar Sr behaviour is also established in other deposits with developing of advanced argillic alteration in the Srednogie Zone and the Rhodopes, e.g. Pesovets, Petelovo, Klisura, Spahievo (Hikov, 2001; 2002; 2004a; 2005) and is probably a widespread phenomenon. All these cases confirm the hypothesis that “the accumulation of Sr is a characteristic feature of the process of advanced argillic

alteration of volcanic rocks” (Hikov, 2004a). A reason for this assumption is the abundance of data on increased concentrations of Sr in advanced argillic zones connected with porphyry copper and high-sulphidation epithermal gold deposits (Schwartz, 1981; Bove, Hon, 1990; McEwan, Rice, 1991; Arribas et al., 1995; Pirajno, 1995; Huston, Kamprad, 2000; Karakaya, Karakaya, 2001), as well as the presence of APS minerals (including svanbergite and svanbergite-woodhouseite s.s.) in the zones of advanced argillic alteration in Bulgaria (Kunov, 1999; Kunov et al., 2000; Georgieva et al., 2002; Hikov, 2004b; Kunov et al., 2006) and abroad (Stoffregen, Alpers, 1987; Muntean et al., 1990; Li et al., 1992; Aoki et al., 1993; Hedenquist et al., 1994, 1998; Dill, 2001; Watanabe, Hedenquist, 2001; Bajnoczi et al., 2003; Deyell et al., 2005; Khashgerel et al., 2008; Voudouris, Melfos, 2013).

Rubidium/Strontium ratio in the altered rocks from Asarel deposit is very characteristic and can be used for geochemical prospecting. Arribas et al. (1995) mentioned similar Rb/Sr ratio in altered rocks from Rodalquilar Au deposit in Spain. Rb/Sr ratio has high values in argillic and sericitic rocks and anomalous low values in advanced argillic rocks and chalcedonic ores. Arribas et al. (1995) presumed that the Rb/Sr ratio has the best potential for identifying promising exploration zones in this deposit. On the other hand, Olade, Fletcher (1975), and Armbrust et al. (1977) discussed the distribution of Rb/Sr ratio in altered zones (except advanced argillic alteration) around some porphyry copper deposits from Canada and Chile. They registered the highest values in the sericitic rocks and proposed Rb/Sr ratio to be used for prospecting of new ore mineralizations. These examples and the data from Asarel give reason to recommend using the Rb/Sr ratio for geochemical prospecting. Anomalously low values of Rb/Sr ratio are typical of advanced argillic zones and suggest high-sulphidation epithermal system, while high values are characteristic of sericitic rocks and could be perspective for prospecting of porphyry copper or low-sulphidation epithermal mineralization. Rb/Sr ratio should be used for geochemical prospecting only together with the whole complex of available geological, petrological, structural and geophysical data.

The study of REE concentration and distribution in hydrothermally altered volcanic rocks from Asarel deposit shows fractionation of these elements in acid and extremely acid conditions. Immobility of LREE and pronounced mobility of MREE and HREE is registered in advanced argillic alteration (both acid-chloride and acid-sulphate) zones. REE mobility depends on the low pH of fluids, high water/rock ratio and the presence of complex agents such as CO_3^{2-} , F^- , Cl^- , and SO_4^{2-} in the hydrothermal fluids (Michard, 1989; Lottermoser, 1992; Fulignati et al., 1989). The main reason for this REE mobility is their ability to form stable complexes. REE form complexes preferentially with Cl^- , F^- and SO_4^{2-} under acid conditions (Wood, 1990; Haas et al., 1995). In order from La to Lu (light-heavy) the stability of

complexes increases. This is a result of decreasing of atomic radius and concentration of electric charge over smaller volume which leads to stronger bonds with the negative ligands (Lottermoser, 1992). Thus, it logically explains the higher mobility of MREE and HREE during advanced argillic alteration. On the other hand, comparative immobility of LREE depends on availability of secondary minerals, such as alunite (Fulignati et al., 1989; Kikawada et al., 2004), APS minerals (Stoffregen, Alpers, 1987; Hedenquist et al., 1994; Arribas et al., 1995; Silaev et al., 2001; Bajnoczi et al., 2003; Khashgerel et al., 2008; Hikov et al., 2010; Chang et al., 2011; Georgieva, Velinova, 2012b), and/or kaolinite (Aja, 1998) which can take them in their lattices. All REE become very mobile in mono-quartzites. This behaviour is connected with their depletion by extremely acid F-bearing hydrothermal fluids and the lack of new minerals, which can accommodate REE.

Thus, alunite and APS minerals control the geochemistry of a number of chemical elements in advanced argillic zones. These are K, Na, Ca, Sr, Ba, P, La, Ce, Nd, part of Pb (Chang et al., 2011; this study), in some cases Ga (Boriskin, 1967; Rytuba et al., 2003), Sc and V (Kashkai, 1970), U and Th (Khashgerel et al., 2008). The trace elements concentrate (e.g. Sr) or are comparatively inert during advanced argillic alteration. On the other hand, rutile concentrates other immobile elements in these highly acid conditions – Ti, V, Sn, W, Nb, Ta, Zr, Hf, partially U, Th, etc.

High concentrations of F and/or Cl are registered in part of the samples from advanced argillic rocks (Table 1) such as the presence of F- and Cl-bearing minerals zunyite and/or topaz (?). Samples from other alteration types also have high F and Cl contents. These are indications of high activity of these elements during hydrothermal alteration, especially during advanced argillic alteration. On the other hand, F has important role in the balance of REE below 350°C (Wood, 1990), as well as of Li (Gavrilenko, Sahonenok, 1986), Ga and Sc (Wood, Samson, 2006) and HFSE (Gavrilenko, Sahonenok, 1986; Rubin et al., 1993; Jiang et al., 2005). At the same time Cl influences on the mobility and transportation in the hydrothermal fluids of Mn, Cr, Ag, Cu, Zn, Pb (Sazonov, 1978; Burnham, 1982; Pirajno, 1992; White, 2009; Sillitoe, 2010). Hence, F and Cl have active participation in the fluid composition, hydrothermal alteration and ore deposition.

CONCLUSIONS

The geochemical study of hydrothermally altered rocks from Asarel porphyry copper deposit shows that using of a single geochemical method is not enough to understand the mobility of trace elements. Complex geochemical techniques are needed to estimate the distribution and the behaviour of trace elements such as detailed study of alteration mineralogy and zoning. Significant changes in the behaviour and distribution of chemical elements took place during advanced argillic

alteration. These changes can be used for studying the geological environment, the evolution of magmatic-hydrothermal systems, and for prospecting of ore mineralizations.

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