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HYDROTHERMAL ALTERATION OF GRANITOID ROCKS AND GNEISSES IN THE DÚBRAVA Sb-Au DEPOSIT, WESTERN CARPATHIANS

MONIKA ORVOŠOVÁ[1], JURAJ MAJZLAN[2,*] and MARTIN CHOVAN[2]

[1]Slovak Museum of Nature Protection and Speleology, Školská 4, 031 01 Liptovský Mikuláš, Slovak Republic
[2]Department of Mineralogy and Petrology, Faculty of Sciences, Comenius University, Mlynská dolina,
842 15 Bratislava, Slovak Republic

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Abstract: Three alteration zones are recognized in hydrothermally altered granitoid rocks at the Dúbrava Sb-Au deposit, Nízke Tatry Mts., Western Carpathians: the outermost chlorite zone, muscovite zone and the innermost illite-carbonate zone. Chlorite replacing biotite originated at temperature about 320 ± 40 °C (according to Cathelineau 1988) and the frequency distribution of Al^{IV} in chlorite suggests its re-equilibration during later hydrothermal events. The muscovite and illite-carbonate zones are superimposed on the chlorite zone. Muscovite appears to be of both magmatic and hydrothermal origin, as deciphered from its TiO_2 content. Hydrothermal muscovite replaces plagioclase and chlorite. In the innermost zone, carbonates and sulphides become abundant, muscovite and feldspars are replaced by illite. Measurements of crystallinity index values of illite gave an estimate of 180–200 °C for the illite-carbonate zone. The altered rocks were enriched in K_2O, H_2O, CO_2, Sb and S and depleted in CaO, MgO, Fe_2O_3, and Na_2O. Minor changes in Al_2O_3 and SiO_2 content are ascribed either to the variations of the composition of the primary magmatic precursor or local redistribution of these elements. Limited data on alteration of amphibole gneisses and migmatites suggest that the main processes were chloritization and illitization; SiO_2 and Na_2O were removed and K_2O added to these rocks.

Key words: Nízke Tatry Mts., granitoids, hydrothermal alteration, illite, muscovite, chlorite.

Introduction

Recent effort to understand the processes governing the formation of the Dúbrava Sb-Au deposit, including detailed mineralogical studies (Chovan 1990), fluid inclusion and stable isotope investigation (Sachan 1989; Chovan et al. 1995) as well as structural data (Sasvári 1997) calls also for a closer inspection of the environment that hosts the ore bodies. This paper presents new data on mineralogical and chemical changes of the wall rocks in the process of alteration induced by hydrothermal fluids responsible for the formation of economic accumulation of antimony and subeconomic amounts of other elements (Au, Cu, Ag).

In the past, little attention was paid to the rock alteration linked to hydrothermal events in the Nízke Tatry Mts. Čillík & Michálek (1983) dealt with the mutual influence of rock environment and hydrothermal mineralization and reported increasing amounts of Pb, Cu, Bi and Ag and decreasing amounts of K, Na, Ca and Mg with increasing Sb. They found that sericitization and silicification is typical for granitoids, while carbonatization, chloritization and saussuritization is characteristic for migmatites. The authors made no attempt to compare the results of chemical analyses with petrographic studies of the rocks. Gubač (1983) mentioned alteration of the rocks hosting W-Au mineralization (Jasenie-Kyslá, Nízke Tatry Mts.).

The Dúbrava deposit is located in the valley of Križianka, on the northern slopes of the Ďumbier part of Nízke Tatry Mts., Western Carpathians, Slovakia. It has been known for a long time. It became an important source of Sb in the 1950's and the exploitation ceased in 1991.

Methods

The studied samples were collected from visible alteration zones of cm to dm thickness around the ore veins of all mineralization stages. Sampling was carried out in four chief mining works in order to detect any horizontal or vertical changes of rock alteration. Additional samples were collected in the periphery of the ore field. The alteration zonality in the scale of meters was studied in a traverse across the alteration envelope of Terézia vein, Martin adit with a sampling distance of 3 m. Changes of mineral composition of the studied rocks were monitored by planimetric analyses of 20 samples. The clay material was size-fractionated by gravity settling. XRD analyses were performed on a DRON diffractometer with Cu Kα radiation and a Ni filter. Oriented samples were prepared by sedimentation of clay suspension (10 mg/cm^2) on glass plates. Samples were analyzed both before and after saturation by ethylene glycol (8 h at 60 °C). Electron microprobe analyses were performed on JXA 840A (CLEOM, Comenius University) (feldspars, biotite, chlorite, illite, Ti-oxides) at 15 kV, 10 nA, standards: albite (Na), anorthite (Ca), spinel (Al), SiO_2 (Si), MgO (Mg), hematite (Fe), adularia (K), MnO (Mn), chromite (Cr) and rutile (Ti); JEOL

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*Current address: Department of Geology, University of California at Davis, Davis 95616, USA; E-mail: jmajzlan@ucdavis.edu

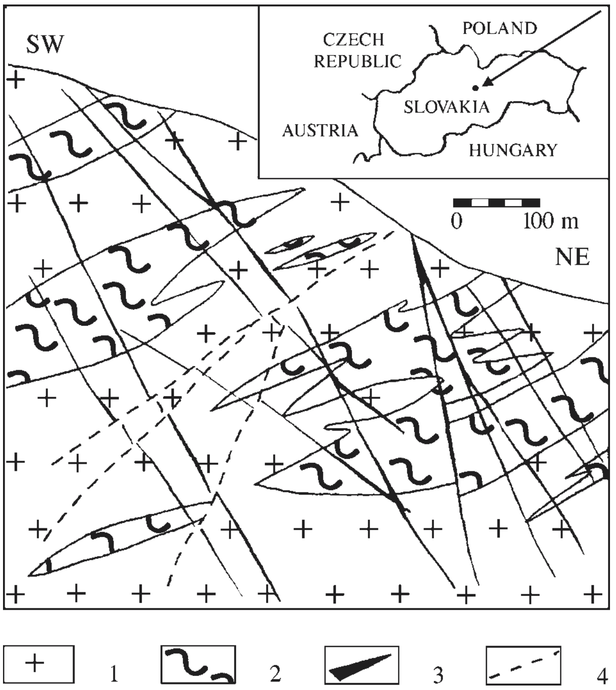

Fig. 1. Sketch cross-section of the Dúbrava deposit (after Michálek 1992). 1 — granitoids, 2 — gneisses and migmatites, 3 — ore veins, 4 — faults. Inset shows localization of Dúbrava deposit in Slovakia.

733 Superprobe (Geological Survey of Slovakia) (muscovite) at 15 kV, 20 nA, standards: albite (Na), wollastonite (Ca), corundum (Al), quartz (Si), MgO (Mg), hematite (Fe). Bulk rock chemistry was determined by wet chemical analysis (major oxides) and combination of AAS and ICP (trace elements). Density of the samples was determined by repeated measurements in pycnometer.

Geological setting and petrography

The Dúbrava deposit is hosted by granitoid rocks; high-grade metamorphic rocks outcrop to the north of the deposit. Xenoliths (up to tens of meters) of migmatites and amphibole gneisses occur as relics of the metamorphic mantle of the granitoids (Fig. 1).

Emplacement of a large pluton composed of granites, granodiorites to tonalites, took place approximately 300 Ma B.P. (Petrík et al. 1994 and references therein). The granitoid rocks represent I-type plagioclase-rich Variscan granitoids (Petrík et al. l.c.) or IS-type granitoids with affinity to I-type granitoids (Kohút 1997). The rock-forming mineral assemblage comprises Mg-biotite, strongly saussuritized plagioclase and quartz (Petrík et al. 1994). Variscan structural scheme was modified by Alpine tectonometamorphic events which caused weak retrograde metamorphism in this area.

The large granitoid pluton of the Nízke Tatry Mts. is built by two principal rock types: the first one (type Ďumbier) being composed of granodiorite to tonalite, the second one (type Prašivá), dominating around the Dúbrava deposit, of granitic to granodioritic composition with porphyric K-feldspars.

Modal composition of the granitoid rocks (Lukáčik 1983) is shown in Fig. 2 (column 1, 2). Mafic minerals are not specified, but according to several authors, biotite greatly predominates. Chemical composition of biotite in unaltered rocks of the pluton falls on the boundary between the fields of Fe- and Mg-biotites (according to Foster 1960, Fig. 3). Magmatic muscovite and amphibole are scarce. Chemical composition of plagioclases and K-feldspars is depicted in Fig. 4. Plagioclases (mostly andesine) are more abundant than K-feldspars. Their composition ranges between $\mathrm{An}_{25\text{-}36}$ (type Ďumbier) and $\mathrm{An}_{17\text{-}34}$ (type Prašivá) (Fig. 4). K-feldspar, the principal phase of the phenocrysts, belongs mostly to microcline (Lukáčik 1983) and contains poikilic inclusions of quartz, biotite and plagioclase. On cooling, plagioclase enclosed in K-feldspar phenocrysts developed albite-rich margins.

Xenoliths of amphibole-biotite gneisses and migmatites underwent alteration similarly as granitoid rocks. Their neosome is compositionally close to biotite granodiorite (quartz, albite–oligoclase, biotite). Paleosome contains amphibole, biotite, plagioclase (albite–oligoclase).

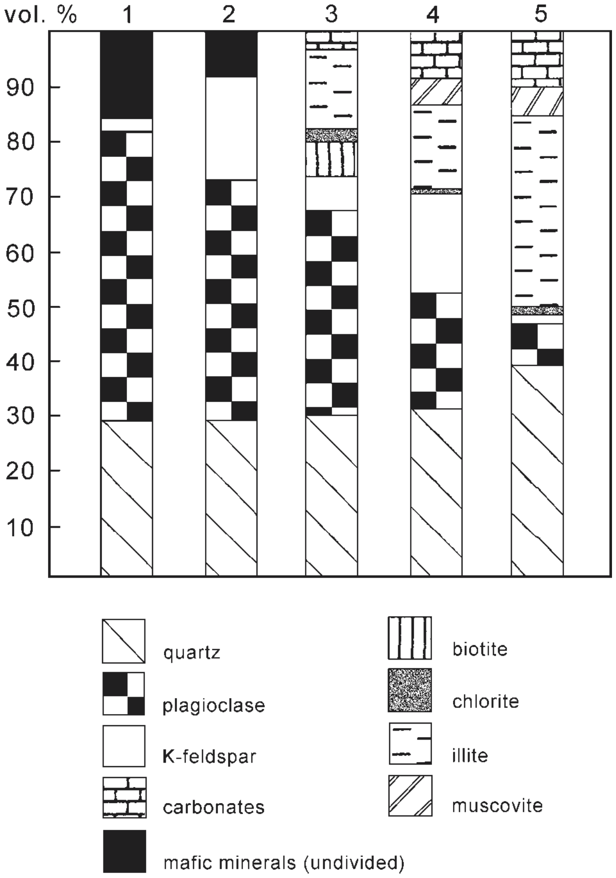

Fig. 2. Modal composition of unaltered granitoid rocks (after Lukáčik 1983, columns 1, 2) and the altered granitoids (columns 3–5) from the Dúbrava deposit. 1 — granodiorite to tonalite (type Ďumbier), 2 — granite to granodiorite (type Prašivá), 3 — chlorite zone, 4 — muscovite zone, 5 — illite-carbonate zone. Lukáčik (1983) did not specify mafic minerals but the dominating one is biotite; amphibole is rare.

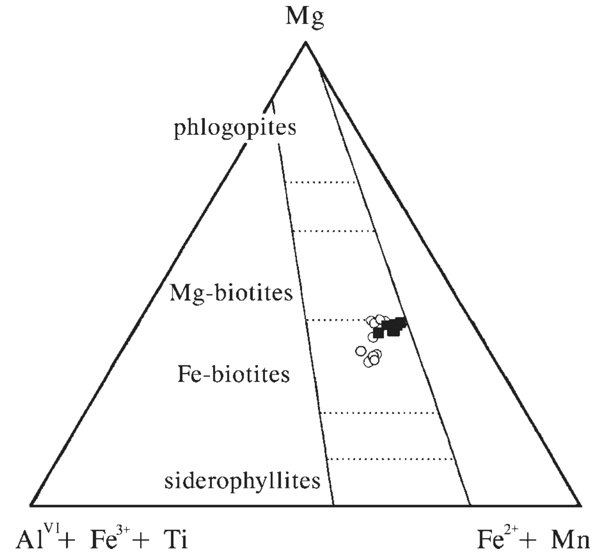

Fig. 3. Composition of biotite in terms of octahedral cations (classification after Foster 1960): biotite from unaltered granitoids (Lukáčik 1983, open circles) and biotite from altered granitoids (chlorite zone, solid squares).

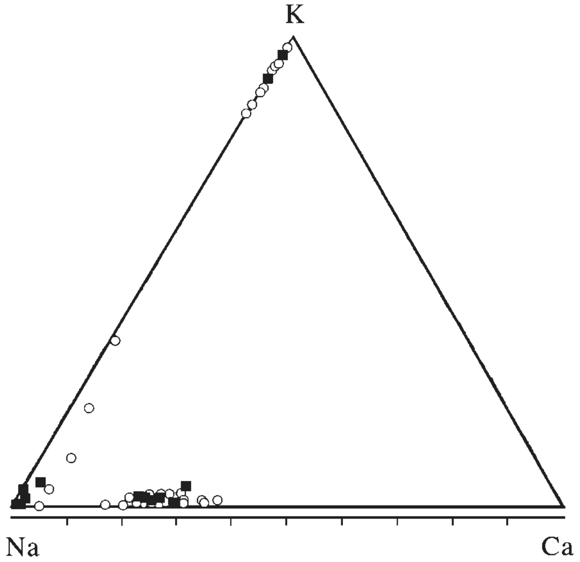

Fig. 4. Composition of feldspars in terms of Na, K, and Ca: feldspars from unaltered granitoid rocks (Lukáčik 1983, open circles) and from altered granitoids (solid squares).

Ore mineralization

The mineralization occurs in veins, stockworks and impregnations in granitoid rocks and xenoliths of metamorphic rocks (Fig. 1). Two major phases of mineral deposition were identified by the mineralogical studies (Chovan 1990): an earlier scheelite phase and later sulphide phase, both of them further subdivided into several stages (Table 1). The distinction between phases and stages is based on mineral assemblages and structural arrangements of the veins bearing different assemblages. Quartz from scheelite, molybdenite and pyrite-arsenopyrite stage contains CO_2-rich and aqueous fluid inclusions with relatively high total homogenization temperature (TH_{tot}) (Table 1). Oxygen isotope data suggest endogeneous source of these fluids. Fluids in quartz of the later stages are richer in dissolved salts and they lack CO_2; contemporaneous decrease in TH_{tot} and salinity and oxygen isotope data indicates the introduction of meteoric waters into the hydrothermal system. Fluids of the last, barite stage contained appreciable amounts of $CaCl_2$. Similar evolution of the fluids is expected in the case of Au-W deposit Jasenie-Kyslá (Nízke Tatry Mts.) where the δD and $\delta^{18}O$ values of water extracted from fluid inclusions in arsenopyrite fall in the field of metamorphic water close to the boundary with the field of magmatic water (Bláha & Bartoň 1991). There is no direct geological or other evidence about the age (Variscan or Alpine) of the Dúbrava deposit. Chovan et al. (1995) argue that the major mineralization event was Variscan, with Alpine remobilization. The Sb-Au deposits of

Table 1: Mineral stages and phases at the Dúbrava deposit and values of THtot and $\delta^{18}O$ of the associated fluid inclusions (after Chovan et al. 1995, completed by new unpubl. data). The stages and phases are listed in successive order.

phases	THtot of fluid inclusions (°C)	$\delta^{18}O$ (water) SMOW
stages		
scheelite		
molybdenite	310-345	+3.5 to +5.1
scheelite	315-355	+3.3 to +5.6
sulfide		
pyrite-arsenopyrite	305-350	+5.5 to +8.5
sulfosalt-stibnite	105-170	-9.3 to −1.7
tetrahedrite	118-162	-3.8 to +1.5
barite	105-158	-4.9 to +1.4

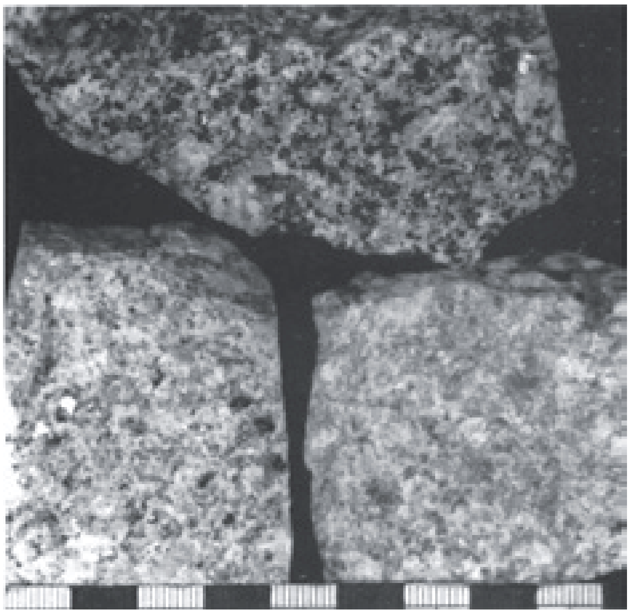

Fig. 5. Macroscopic appearance of altered rocks from chlorite zone (top), muscovite zone (bottom left) and illite-carbonate zone (bottom right). Scale in cm.

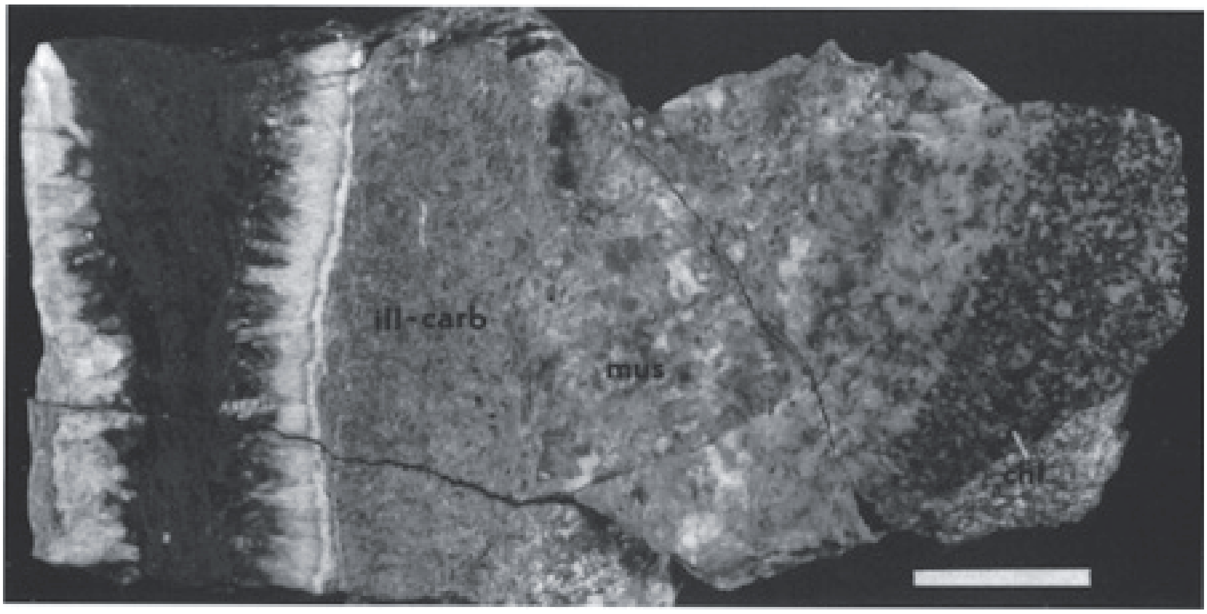

Fig. 6. Alteration halo of a quartz-stibnite vein (in the left part of the photograph). **ill-carb** — illite-carbonate zone, **mus** — muscovite zone, **chl** — chlorite zone. Scale bar = 2 cm.

Table 2: Electron microprobe analyses of biotite, muscovite, chlorite and illite from the altered rocks in Dúbrava. Analyses of chlorite recalculated on the basis of 14 oxygen atoms, analyses of other minerals on the basis of 22 oxygen atoms.

Sample	**A-9**	**A-45**	**A-23**	**A-7**	**A-21**	**A-9**	**A-45**	**A-22**	**A-16**	**A-14**	**A-7**	**A-27**	**A-27**	**A-28**	**A-37**	**A-38**
avg. of	**1**	**3**	**1**	**4**	**4**	**4**	**3**	**2**	**4**	**4**	**4**	**2**	**1**	**1**	**4**	**9**
	Bt	Bt	Bt	Chl	Chl	Chl	Chl	Chl	Ms	Ms	Ms	Ms	Ms	Ill	Ill	Ill
SiO_2	36.85	35.34	36.85	26.86	26.84	25.29	27.03	26.35	46.27	45.24	46.19	45.90	45.92	48.04	51.43	48.54
TiO_2	3.10	2.89	3.10	0.09	0.10	0.08	0.13	0.25	0.57	0.66	1.55	1.24	2.12	0.11	0.05	0.16
Al_2O_3	16.30	16.53	16.30	20.82	21.05	21.19	19.03	21.27	29.29	33.67	31.06	31.24	30.09	34.24	30.32	33.41
Cr_2O_3	0.06	0.10	0.07	n.a.	n.a.	n.a.	n.a.	n.a.	0.00	0.00	0.00	0.00	0.00	0.08	0.06	0.02
FeO	20.64	19.97	20.64	28.15	20.88	25.40	24.83	22.82	5.63	3.47	4.27	4.27	4.01	2.50	1.75	2.87
MnO	0.41	0.90	0.41	0.11	0.48	0.51	0.61	0.60	0.00	0.00	0.00	0.00	0.00	0.02	0.04	0.05
MgO	9.47	9.69	9.47	11.35	17.88	13.70	13.92	15.43	2.29	0.61	0.98	0.98	1.11	0.29	1.84	1.30
CaO	0.00	0.02	0.01	0.08	0.03	0.08	0.06	0.05	0.00	0.00	0.00	0.00	0.00	0.05	0.10	0.03
Na_2O	0.05	0.15	0.06	0.01	0.00	0.02	0.01	0.01	0.15	0.48	0.28	0.30	0.25	0.25	0.26	0.36
K_2O	9.61	9.66	9.62	0.30	0.06	0.11	0.45	0.52	11.47	11.16	11.16	11.14	11.11	10.93	9.60	8.52
Total	96.49	95.24	96.53	87.76	87.31	86.39	86.07	87.28	95.67	95.29	95.49	95.07	94.61	96.51	95.43	95.27
Si^{IV}	5.59	5.45	5.58	2.86	2.77	2.71	2.90	2.76	6.33	6.13	6.27	6.26	6.29	6.34	6.76	6.41
Al^{IV}	2.41	2.55	2.42	1.14	1.23	1.29	1.10	1.24	1.67	1.87	1.73	1.74	1.71	1.66	1.24	1.59
T site	8.00	8.00	8.00	4.00	4.00	4.00	4.00	4.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Al^{VI}	0.50	0.46	0.49	1.47	1.33	1.40	1.31	1.39	3.06	3.50	3.24	3.28	3.15	3.67	3.46	3.60
Ti^{VI}	0.35	0.34	0.35	0.01	0.01	0.01	0.01	0.02	0.06	0.07	0.16	0.13	0.22	0.01	0.00	0.02
Cr	0.01	0.01	0.01	n.a.	n.a.	n.a.	n.a.	n.a.	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00
Fe^{3+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe^{2+}	2.62	2.58	2.62	2.51	1.80	2.28	2.23	2.00	0.64	0.39	0.48	0.49	0.46	0.28	0.19	0.32
Mn^{2+}	0.05	0.12	0.05	0.01	0.04	0.05	0.06	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Mg	2.14	2.23	2.14	1.80	2.75	2.19	2.23	2.41	0.47	0.12	0.20	0.20	0.23	0.06	0.36	0.26
O site	5.67	5.73	5.66	5.80	5.93	5.93	5.84	5.87	4.23	4.09	4.08	4.09	4.06	4.02	4.03	4.21
Ca	0.00	0.00	0.00	0.01	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.00
Na	0.01	0.04	0.02	0.00	0.00	0.00	0.00	0.00	0.04	0.13	0.07	0.08	0.07	0.06	0.07	0.09
K	1.86	1.90	1.86	0.04	0.01	0.02	0.06	0.07	2.00	1.93	1.93	1.94	1.94	1.84	1.61	1.44
A site	1.87	1.95	1.88						2.04	2.05	2.01	2.02	2.01	1.91	1.69	1.54

Nízke Tatry Mts. appear to be genetically close to the Variscan Sb-Au mineralization of Massif Central, Iberian massif (e.g., Boiron et al. 1989, 1996; Ortega et al. 1996) and elsewhere.

Results

There are no unaltered wall rocks left in the Dúbrava deposit. Field work, petrographic observation, mineralogical studies and chemical analyses supplied evidence of hydrothermal alteration of the studied rocks. Samples collected in the periphery of the ore field show also weak alteration. Thickness of the inner alteration zones reaches centimetres to decimeters. The alteration envelope is best developed around the major veins with economic accumulation of metals, but it is found also around minor (few cm thick) veinlets or even fractures without ore mineralization. The study of alteration at the scale of meters was limited due to strong tectonic fracturing (and consequent alteration) in the surrounding of the veins. In the thin sections, secondary trails of CO_2-rich as well as aqueous fluid inclusions, corresponding to the two major phases of deposit formation, can be found.

Changes of mineral composition of granitoids

The least altered rocks are greenish in color, equigranular, medium- to coarse-grained with occasional transitions into porphyric types (Figs. 5, 6). Illitization of plagioclase in this zone is weak; illite represents only about 12 vol. % of the feldspar (Fig. 2). Acidic reaction rims between plagioclase and K-feldspar contain no illite (Fig. 7a). Chessboard albite and various forms of pertites are common in the K-feldspar phenocrysts but they show no signs of alteration due to hydrothermal metasomatic processes. The Mg/(Mg + Fe) ratio of biotite in the altered rocks (0.45–0.48) is identical to the ratio for biotite from unaltered granitoid rocks (0.45–0.49) (Table 2, Fig. 3). Biotite is partially or completely converted to chlorite (brunsvigite, ripidolite, according to Foster 1962) (Figs. 7b, 8a, Table 2) and needle-like crystals or fine-grained aggregates of rutile, rarely also epidote or sphene. Chlorites (Mg/(Mg + Fe) = 0.39–0.64) are formed exclusively at the expense of biotite. Chemical composition of feldspars from altered samples and unaltered rocks (Lukáčik 1983) does not differ (Fig. 4).

Decomposition of biotite and chlorite leads to bleached appearance of the rocks (Figs. 5, 6) closer to the contact with ore veins. The rocks appear as equigranular, medium- to coarse-grained. Illitization is still not intensive and the proportion of illite does not increase (Fig. 2). Chlorite is preserved only rarely and is mostly replaced by muscovite with inherited cleavage planes clearly marked by fine-grained aggregates of Ti-oxides, identified by electron microprobe analyses. Sporadic epidote and sphene are products of decomposition of biotite and plagioclase. Minute anhedral grains of Fe-dolomite and calcite become more abundant, replacing plagioclase and chlorite. K-feldspars are still relatively resistant to alteration.

Strongly altered rocks, confined to immediate vicinity of ore veins, are grayish or white in color, medium to fine-grained (Figs. 5, 6). Relics of muscovite flakes, replaced by illite (Fig. 7c), Ti-oxides, epidote and carbonates represent the original biotite crystals. In thin sections, muscovite and illite were distinguished on the basis of crystal size; fine-grained aggregates were considered to be illite and separate large flakes muscovite. Other rock-forming minerals, except of quartz, are almost totally transformed to illite which represents up to 33 vol. % of the rock (Fig. 2). Chessboard albite and pertites in K-feldspars are preferentially replaced by illite. Increasingly abundant carbonates form aggregates of veinlets in plagioclase, less in K-feldspars. Strongly altered rocks bear larger quantities of euhe-

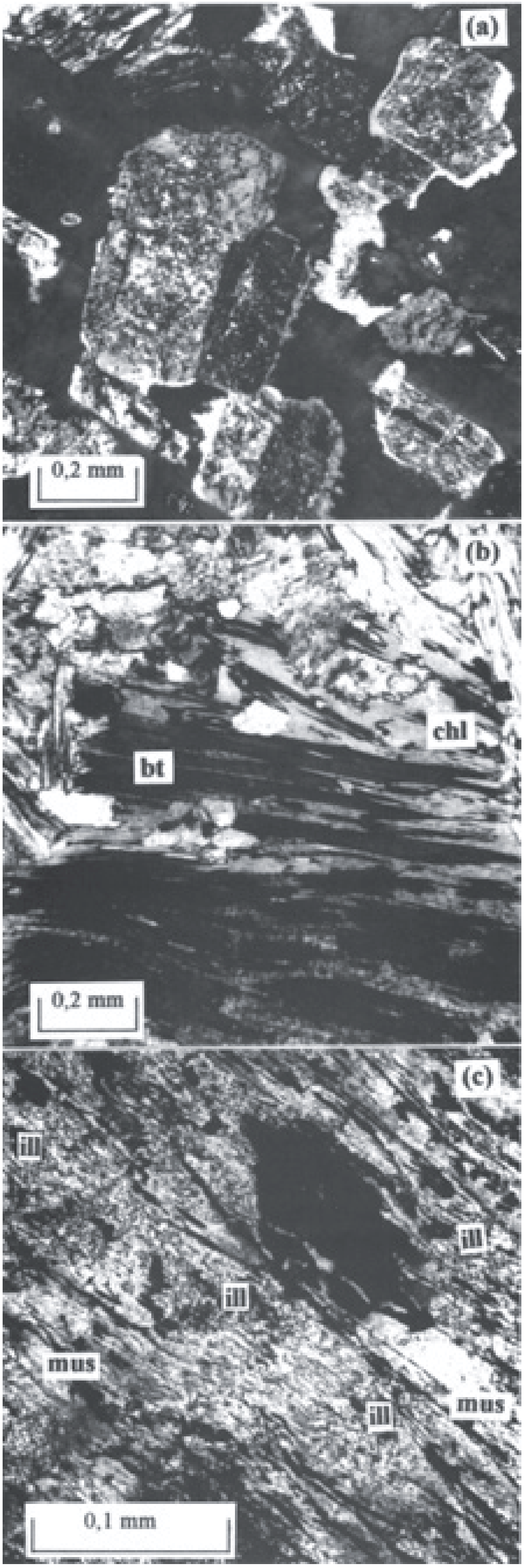

Fig. 7. **(a)** partially sericitized plagioclase crystals in unaltered K-feldspar, note the unaltered rims on the plagioclase crystals; **(b)** biotite — ***bt*** flakes partially altered to chlorite — ***chl***; **(c)** muscovite — ***mus*** replaced by fine-grained aggregate of illite — ***ill***.

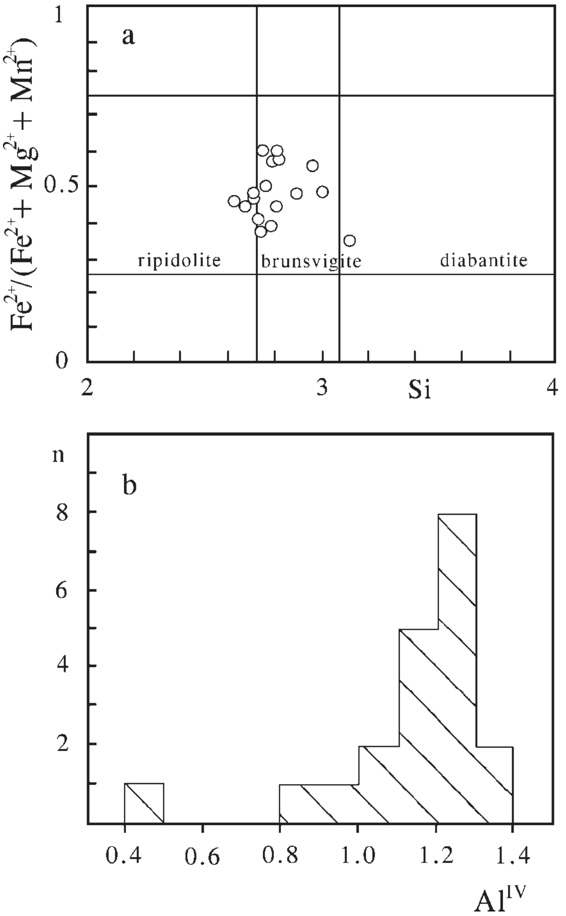

Fig. 8. a — chemical composition of chlorites in the classification diagram of Foster (1962); **b** — histogram of Al^{IV} content in chlorites.

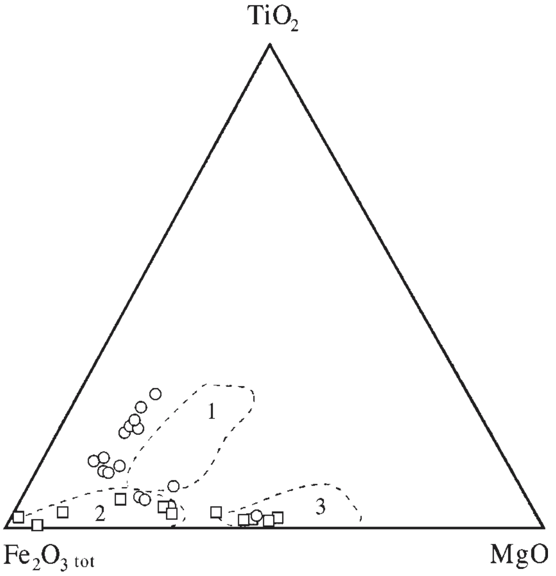

Fig. 9. Ternary diagram of TiO_2, Fe_2O_3, and MgO in muscovite (circles) and illite (squares) from the altered rocks from the Dúbrava deposit. Fields after Monier et al. (1984): 1 — magmatic muscovite, 2 — late to post-magmatic muscovite, 3 — hydrothermal illite.

dral crystals, veinlets and impregnations of pyrite, arsenopyrite, and stibnite.

Changes of mineral composition of migmatites

The collected migmatite samples do not display as profound mineral changes as in the case of granitoid rocks. The chief processes induced by hydrothermal fluids are chloritization and illitization. Muscovitization of mafic minerals was not observed. Alteration intensity may be assessed according to the degree of amphibole preservation and the variable volume proportion of the secondary minerals.

Changes of chemical composition of granitoids

Investigation of chemical composition of the rocks is another way of alteration assessment. In this study, alteration index (A.I. = $(MgO + K_2O) / (Na_2O + K_2O + CaO + MgO)$) defined by Hashiguchi et al. (in Vivallo 1987) was found to be a useful tool. The degree of alteration estimated from petrographic study correlates well with the A.I. The least altered rocks are typical of A.I. < 50, while the most altered ones reveal A.I. > 60, with a maximum at more than 80.

Chemical analyses of the altered rocks are listed in Table 4. The first 16 analyses (A-9 to A-11) represent granitoid rocks and are arranged, with an exception of A-9, in the order of increasing A.I. The sample A-9 was selected as the „least altered one“ according to petrographic observation, (the degree of biotite preservation), even if it does not hold the lowest A.I. value. The last three analyses are migmatite samples, with increasing degree of alteration from A-23 to A-34. Approaching to the ore veins, density of the samples slightly decreases and then increases sharply due to the abundant sulfide grains in the immediate vicinity of the veins.

Discussion

The principal wall-rock alteration products in the Dúbrava Sb-Au deposit are chlorite, muscovite and illite, together with lesser amounts of rutile, epidote, Fe-dolomite, calcite, and other minerals formed by decomposition of biotite, plagioclase and K-feldspar. Progressive alteration caused transformation of original magmatic biotite to chlorite, muscovite and illite. The three latter sheet silicate minerals are abundant and typical for a specific alteration zone and govern the textures and color of the rocks. Three zones of alteration are recognized in the Dúbrava deposit:

I. chlorite zone,
II. muscovite zone,
III. illite-carbonate zone.

Chlorite is preserved only in the most external (chlorite) zone. Recently, De Caritat et al. (1993) gave critical evaluation of available empirical and thermodynamic chlorite thermometers and concluded that none of them performs satisfac-

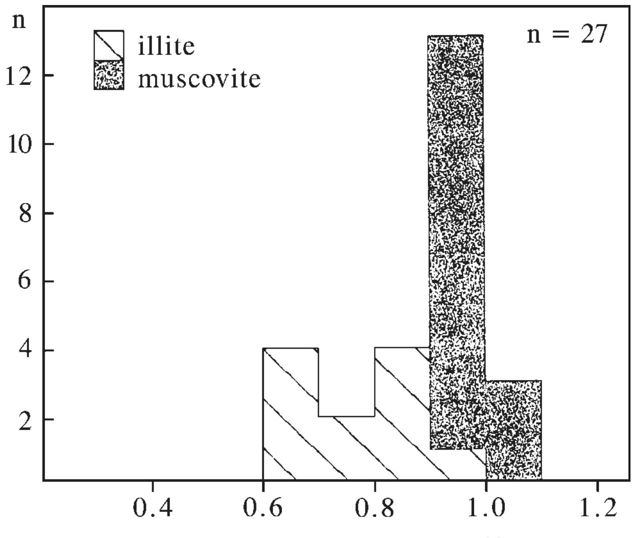

Fig. 10. Distribution of $K/O_{10}(OH)_2$ in muscovite and illite from the altered rocks.

torily in the full range of chlorite composition, bulk rock mineralogy and P-T conditions examined. Empirical thermometers, such as the one developed by Cathelineau (1988) are valid only for specific geological environment and produce large errors if used in geochemically different environments. Later thermal events may also override the original chemistry of chlorite, thus affecting any thermometric data. Although there was undoubtedly a later event related to the formation of sulfidic stages the studied chlorite seem to record, at least partially, action of the higher thermal fluids linked to the older mineralization stages. In the case of alteration, chlorite may inherit compositional features of its precursor. Application of chlorite thermometers to the samples from Dúbrava gives wide range of formation temperatures, summarized in Table 3. Asymmetry of Al^{IV} frequency distribution (Fig. 8b) in chlorite suggests re-equilibration of studied chlorite during later mineralization stages. We believe that the calculated average temperature 320 ± 40 °C (Cathelineau 1988; Jowett 1991; Table 3) is reasonable when compared to the previous results of fluid inclusion investigation (Chovan et al. 1995).

Several authors investigated reactions of rock-forming minerals under hydrothermal conditions. Ferry (1979) reports breakdown of biotite to chlorite, sphene and release of silica, K^+ and Na^+ into the fluid. In their experimental work with iron chloride complexes, Fein et al. (1992) found that no annite was formed in the presence of sulfur in agreement with the data of Hammarback & Lidqvist (in Fein et al. 1992) who suggested that annite component is destabilized by sulfur. Destabilization of biotite and amphibole by S-rich fluid is reported also by Tso et al. (1979) and Popp et al. (1977). Furthermore, if the fluid contains As-bearing complexes, the reaction will proceed according to Heinrich & Eadington (1986) as follows:

$$\text{biotite} + \text{chlorite} + H_3AsO_4 + H_2S \rightarrow$$
$$\rightarrow \text{muscovite} + \text{quartz} + \text{arsenopyrite} + \text{water} + O_2$$

$$\text{K-feldspar} + \text{chlorite} + H_3AsO_4 + H_2S \rightarrow$$
$$\rightarrow \text{muscovite} + \text{quartz} + \text{arsenopyrite} + \text{water} + O_2$$

Bryndzia & Scott (1987) mention also destabilization of Fe-chlorite by sulfidation, although at temperatures and pressures higher than those assumed for the Dúbrava deposit. All these reactions may account for release of silica in the hydrothermal fluid and development of impregnations of pyrite and arsenopyrite in the altered rocks.

Muscovite is found in all alteration zones, but it dominates only in the muscovite zone. The least altered rocks contain muscovite flakes only along grain boundaries of plagioclases; in the course of alteration, muscovite replaces chlorite and plagioclase. Electron microprobe analyses (Table 2) revealed that the textural variety of muscovite found in the least altered samples with still preserved biotite contains the largest amounts of Ti. This muscovite is considered to be of magmatic or late magmatic origin (Fig. 9). Muscovite that obviously replaces chlorite contains less Ti, representing the product of hydrothermal activity. Fig. 9 depicts comparison of chemical composition of muscovite from Dúbrava with compositional fields of magmatic and hydrothermal muscovite in the Millevaches Massif outlined by Monier et al. (1984). Position of our analyses outside of the magmatic muscovite field is most probably due to differences in bulk rock chemistry; the general trend is clearly preserved, however. In more altered samples, distinction between magmatic and hydrothermal muscovite, based exclusively on the petrographic observations, becomes ambiguous. Beside TiO_2, Monier et al. (1984) showed that magmatic muscovites exhibit a higher $Na_2O/(Na_2O + K_2O)$ ratio (0.07–0.12) while hydrothermal white micas are characterized by substantially lower ratio (0.02–0.06). On the other hand, in their discrimination of magmatic and hydrothermal muscovites in granites, Villa et al. (1997) found no differences between the two groups in Na_2O and K_2O content, although the difference in TiO_2 concentration is obvious. A little variation in $Na_2O/(Na_2O + K_2O)$ ratio with changing TiO_2 concentration in muscovite was observed also in the studied samples from the Dúbrava deposit (Table 2).

Illite from Dúbrava is characterized by lower content of $K/O_{10}(OH)_2$ and Al^{IV} than muscovite, FeO_{tot} content up to 3 wt. % and low TiO_2 content (Table 2, Fig. 9), comparable to the published data on illite composition (Środoń & Eberl 1984). The $K/O_{10}(OH)_2$ content shows distribution with two maxima between 0.6–0.7 and 0.8–0.9 $K/O_{10}(OH)_2$ while muscovite contains 1.02 ± 0.02 (1σ) $K/O_{10}(OH)_2$ (Fig. 10). It is not clear whether the analyses correspond to mixed-layer illite-smectite or merely to a mixture of illite with later smectite. The end-member illite was found to contain 0.88 (Yates & Rosenberg 1997) or 0.85 (Aja 1991) $K/O_{10}(OH)_2$. Aja (1991) implies also

Table 3: Estimated temperature of chlorite formation according to various chlorite thermometers.

	range mean (1σ)
Cathelineau (1988)	215–376 319(39)
Kranidiotis & MacLean (1987)	135–195 179(14)
Jowett (1991 in De Caritat et al. 1993)	217–380 324(39)

the existence of stable solubility-controlling phase with 0.69 $K/O_{10}(OH)_2$.

Table 5 lists the results of XRD analyses of the most altered granodiorites, performed to determine their mineral composition and the crystallinity index (CI) value. The measured values, compared to the data of Šucha & Eberl (1992) gave an estimate of illite crystallization interval of 180–200 °C. The CI values are similar to those measured for hydrothermal illite in Silverton caldera by Eberl et al. (1987) who determined crystallization temperature from δH and $\delta^{18}O$ data to 170–320 °C. Some XRD patterns reveal the presence of minor amounts of smectite which probably originated during final, lower, thermal stages of the alteration process.

Mylonite zones, apparently reactivated during the Alpine orogeny, including the Ľubelská fault, a major structure running throughout the deposit, contain mostly illite and traces of smectite and kaolinite.

The isocon method of Grant (1986) was adopted in the calculation of gains and losses during wall-rock alteration. Field observations suggest little or no volume change during alteration, but its quantification is not feasible. The isocons defined for no mass change are almost identical with those for constant volume. The solution of Gresens' (1967) equation gave no single datum for the volume change for the pairs of the least altered sample and other analyzed samples, a considerable scatter of values was obtained instead. The isocons for constant alumina imply volume changes in range between −8.2 to +9.5 %, but aluminum needs not to be immobile (cf. Robert & Brown 1986; Boiron et al. 1989), although in other cases it seems to be (Ferry 1985; MacLean & Kranidiotis 1987; Ortega et al. 1996). Enrichment or depletion was quantified on the basis of constant volume assumption.

MacLean & Kranidiotis (1987) advise investigation of the relationship of pairs of elements, where one of them serves as a reference and is shown or considered to be immobile. If the data points for the two elements form a linear array with high positive correlation passing through the origin then the second element is also immobile, provided that the two elements are not decoupled geochemically. The most suitable reference element in most cases appears to be zirconium. High positive correlation coefficients were found only in the case Zr–TiO_2 (r = 0.92, Fig. 11a) and Zr–Sc (r = 0.83, Fig. 11b), suggesting that these three elements behaved as immobile throughout the alteration process. Contrary to this, rutile is a common constituent of the pyrite-arsenopyrite assemblage of hydrothermal veins and the trends for both elements (TiO_2, Sc) are but a copy of the magmatic trends (Figs. 11a, b). Investigation of the relationships Zr–Al_2O_3 (Fig. 11c) and Zr–K_2O (Fig. 11d) shows that they follow the magmatic trends as well, with an evident gain of K_2O (Fig. 11d). The application of this method seems to be questionable. We suppose that TiO_2 was released from primary magmatic minerals (biotite) but its migration was limited. We are unable to judge the degree of Sc mobility.

Figs. 12a–g demonstrate gains and losses in the analyzed samples arranged in the order of increasing alteration index. Variations in alumina and silica content (Figs. 12a,b) are ascribed either to the variable chemical composition of the magmatic precursor, or, more probably, to local redistribution of Al_2O_3 and SiO_2. Chlorite is occasionally found in the fractures of the vein quartz, indicating extraction of Al from the ambient rocks into the veins. Therefore, calculations of chemical changes on the basis of constant Al_2O_3 were avoided and the constant volume approach was used instead.

From the change in mineralogy across alteration zones it is obvious that K_2O, H_2O, Sb, S were added to the rocks during alteration, whereas CaO, Na_2O, MgO, Fe_2O_3 were removed (Figs. 12c–g). Conversion of biotite to chlorite in the chlorite

Table 4: Bulk chemical composition of altered rocks from the Dúbrava deposit. Oxides in wt.%, trace elements in ppm. LOI = loss on ignition, D = density, A.I. = alteration index (see text). Analyses of altered granitoids are arranged in the order of increasing A.I.

	A-9	**A-38**	**A-44**	**807**	**806**	**A-7**	**A-27**	**A-37**	**A-16**	**A-14**	**A-32**	**A-6a**	**A-25**	**A-10**	**1A**	**A-11**	**A-23**	**A-22**	**A-34**
	granitoids																**migmatites**		
SiO_2	66.06	67.88	68.45	66.51	68.72	65.69	64.05	54.67	69.05	71.20	64.50	64.85	66.80	70.08	65.87	68.62	56.53	54.10	51.06
Al_2O_3	15.28	15.04	14.57	14.79	15.01	15.70	16.46	14.69	14.49	14.27	16.97	16.57	16.23	15.90	17.26	17.09	15.06	15.54	14.69
Fe_2O_3	3.70	3.29	3.36	4.11	2.93	2.44	3.33	6.45	2.22	3.28	2.14	3.94	2.99	1.58	3.45	2.00	8.05	9.20	8.13
TiO_2	0.582	0.470	0.521	0.676	0.465	0.614	0.549	0.580	0.380	0.188	0.514	0.304	0.513	0.570	0.375	0.480	0.916	1.089	0.971
CaO	2.93	3.06	2.51	2.57	2.23	2.55	1.68	4.51	1.35	0.32	2.49	0.67	1.48	0.65	1.06	0.83	5.36	5.32	6.47
MgO	1.55	1.24	1.38	1.89	1.29	1.26	1.53	3.36	0.79	0.52	1.53	1.29	1.22	0.73	1.20	0.89	5.33	5.26	5.35
MnO	0.069	0.049	0.045	0.060	0.043	0.061	0.107	0.230	0.057	0.098	0.037	0.150	0.176	0.021	0.140	0.067	0.146	0.182	0.150
P_2O_5	0.37	0.35	0.24	0.35	0.20	0.41	0.25	0.63	0.16	0.23	0.21	0.26	0.22	0.27	0.10	0.23	0.43	0.79	0.47
Na_2O	3.53	3.67	3.37	3.48	3.38	2.78	2.38	0.62	2.52	2.77	1.09	2.43	1.13	2.00	1.21	0.45	3.20	2.67	1.78
K_2O	3.36	2.72	2.62	2.73	3.27	4.13	4.24	4.08	4.85	4.43	4.42	4.31	4.46	5.04	4.55	5.33	2.39	2.44	2.63
SO_3	0.18	0.13	0.09	0.06	0.08	0.14	0.69	2.77	0.94	0.59	0.27	0.13	1.21	0.15	0.45	0.27	0.06	2.07	1.41
LOI	1.75	1.73	2.66	2.13	2.18	3.43	4.99	9.53	2.75	2.54	5.73	4.49	4.62	2.48	4.85	3.69	1.59	2.37	7.43
H_2O	0.27	0.28	0.28	0.26	0.18	0.25	0.30	0.35	0.25	0.28	0.45	0.43	0.31	0.44	0.42	0.30	0.32	0.23	0.34
Total	99.18	99.50	99.73	99.30	99.72	99.07	99.57	99.35	98.65	99.85	99.90	99.26	99.84	99.33	100.10	99.68	99.00	98.96	99.13
Zn	63.95	69.95	54.88	87.37	41.95	37.28	32.00	24.95	20.40	15.83	16.74	21.88	26.04	33.84	34.86	22.13	119.20	158.30	107.30
Rb	118	85	87	95	103	143	163	192	135	191	161	174	224	142	193	214	83	127	130
Sc	9.456	8.178	9.445	10.13	9.037	9.324	8.178	11.060	5.776	5	9.148	5	7.903	5.975	7.407	6.129	23.830	24.610	27.670
Co	4.786	4.711	3.396	5.537	3.044	3.452	4.885	12.090	3.479	5.461	2.709	1	2.78	2.861	1	1.763	15.990	12.430	19.630
Ni	7.761	5.836	4.645	7.021	3.921	3.235	3.778	20.450	2.562	9.886	1.716	4.455	1.582	3.552	1.468	4.478	12.850	6.271	25.810
Sr	730	610	560	680	500	490	280	270	610	160	250	280	300	240	320	230	1610	1350	890
Y	12	13	9	12	12	14	13	25	6	10	8	12	12	17	9	16	25	34	29
Zr	237	217	195	250	179	230	196	218	175	110	193	89	177	192	172	173	228	288	251
Ba	1990	1040	1000	1420	1380	4010	420	820	4750	460	390	1930	1290	2020	550	290	2040	1530	900
D	2.707	2.703	2.714	2.709	2.696	2.791	2.713	2.738	2.659	2.682	2.732	2.751	2.731	2.706	2.744	2.723	2.759	2.798	2.789
A.I.	0.432	0.370	0.405	0.433	0.448	0.503	0.587	0.592	0.593	0.616	0.624	0.644	0.685	0.685	0.717	0.829			

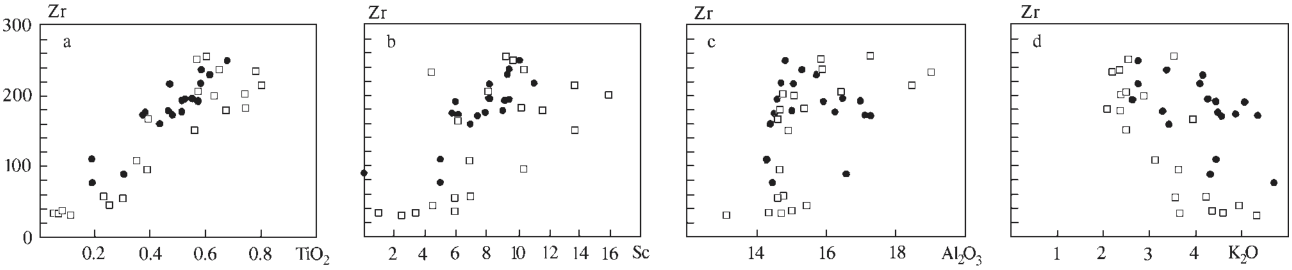

Fig. 11. Plots of Zr vs. TiO_2, Sc, Al_2O_3, and K_2O for unaltered granitoids (Cambel and Janák, unpubl.data, solid circles) and altered granitoids from the Dúbrava deposit (open squares). Zr and Sc in ppm, oxides in wt. %.

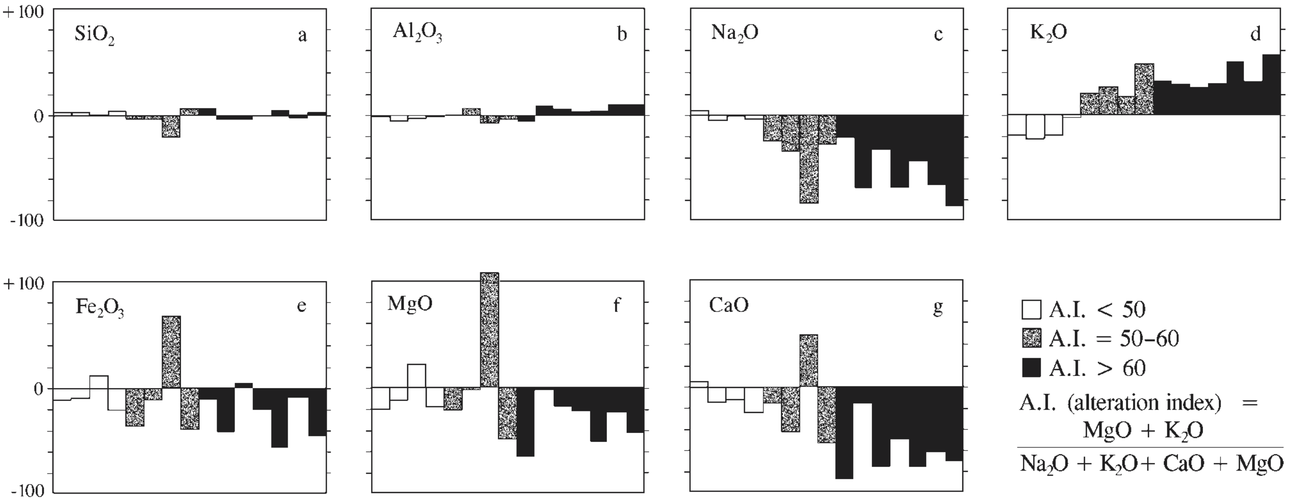

Fig. 12. Percentage gains and losses of oxides in altered granitoid rocks from the Dúbrava deposit based on data listed in Table 4 arranged in order of increasing alteration index. The calculation was performed from 15 samples, the sample A-9 was used for normalization.

zone is responsible for K_2O loss in the less altered samples (Fig. 12d). Illitization accounts for most of the gain of K_2O and H_2O. Loss of Na_2O (Fig. 12c) and CaO (Fig. 12g) is due to decomposition of plagioclases. MgO (Fig. 12f) and Fe_2O_3 (Fig. 12e) were removed during destruction of biotite and chlorite. Fixation of Ca, Mg and Fe in carbonates was not sufficient to counterpart their release; only a single anomalous sample (A-37) shows a positive change (gain) for these elements (Figs. 12e–g). The samples were not analyzed for CO_2, but according to abundant occurrence of carbonates, the rocks were also enriched in CO_2.

Table 5. Crystallinity index values of illite from the altered rocks from the Dúbrava deposit (in °2Q).

Sample	CI (air dried)	CI (EG)
A-37 (1)	0.55	
A-37 (2)	0.40	
A-10	0.44	0.38
A-27	0.22	0.225
A-6A	0.46	0.38
A-5	0.36	0.35
A-101	0.46	0.415
A-100	0.62	0.41
A-8	0.36	0.385
A-25	0.52	0.42
829	0.70	0.65

Evaluation of the element migration in migmatites is limited due to few analyzed samples. It seems that SiO_2 and Na_2O were removed and K_2O added to these rocks (Table 4). Minor losses were determined also in the case of Fe_2O_3, MgO and CaO. The same fluids drove hydrothermal alteration of both granitoids and migmatites and therefore the differences in alteration patterns are caused only by the variability of the primary material.

Conclusions

Changes of chemical and mineralogical composition of rocks altered by hydrothermal fluids at the Dúbrava Sb-Au deposit, Nízke Tatry Mts. enabled to distinguish three zones of alteration: I. chlorite zone (outermost), II. muscovite zone, III. illite-carbonate zone (innermost).

Every wall rock sample from the deposit represents an altered rock. Increasing degree of alteration results in progressive decomposition of plagioclase, K-feldspar and complete disappearance of biotite. Primary magmatic minerals and textures are completely erased in the most internal alteration zone.

The presented data indicate a temperature decrease from the external chlorite zone (320±40 °C, chlorite thermometry) toward the inner zone rich in illite and carbonates (180–200 °C, crystallinity index). The initial stages of alteration bore pervasive character, altering mostly biotite in large volumes of rocks within the ore field. Muscovite and illite-carbonate zones are superimposed on the most external chlorite zone. They are a product of action of cooler thermal fluids whose circulation was restricted to open tectonic structures and channelways. Gradual sealing of the walls of the veins and temperature decrease led to isolation of external chlorite zone and preservation of its mineral assemblage even during later events.

In the course of alteration, the rocks were enriched in K_2O, H_2O, CO_2, Sb, S and depleted in CaO, Na_2O, MgO and Fe_2O_3 (Figs. 12c–g). Local redistribution and/or variation in the chemical composition of the primary magmatic precursor caused small changes in Al_2O_3 and SiO_2 content (Figs. 12a, b). Zr, TiO_2 and Sc seem to be the least mobile elements, although rutile appears in pyrite-arsenopyrite assemblage of the quartz veins.

Similar features of alteration accompanying the ore mineralization are expected, according to our observations, also in other Sb-Au deposits (Magurka, Dve Vody) in the Nízke Tatry Mts.

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