Chapter 5

Distribution and Origin of Clay Minerals During Hydrothermal Alteration of Ore Deposits

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Additional information is available at the end of the chapter

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1. Introduction

Hydrothermal alterations of host rocks (granites and metasediments) connected with origin Sn-W and U deposits are often accompanied by origin of chlorite, clay minerals and white mica (muscovite, hydromuscovite, phengite) [1, 2, 3, 4, 5, 6, 7]. Clay minerals originated usually in last stages of these alterations, when temperature of hydrothermal fluids is in range of 50–200 ºC. In area of Central European Variscan belt (Bohemian Massif) occur a few Sn-W- and U-ore deposits in which are evolved altered rocks with highly interested chlorite, clay minerals and white mica assemblages (Fig. 1). This paper is concentrated on description and discussion of chloritization and argillization, originated during alteration of host rocks series at selected Sn-W and U ore deposits in the area of the Bohemian Massif (Czech Republic).

2. Geological background

The Sn-W greisen deposits are connected with topaz-granite stocks in the Saxothuringian Zone of the Bohemian Massif (Krásno–Horní Slavkov ore district, Cínovec). The Krásno–Horní Slavkov ore district comprises topaz-bearing granite stocks evolved along the southeastern margin of the Krudum granite body in the Slavkovský les Mts. area (Fig. 2). The inner structure of these stocks (Hub, Schnöd and Vysoký Kámen) is well stratified, comprising partly greisenized topaz-albite granites, leucocratic topaz-albite granites and layers of alkali-feldspar syenites. In upper parts of the Hub and Schnöd stocks are evolved topaz-mica greisens, accompanied by partly greisenized topaz-albite granites and distinctly argillitized topaz-albite granites. The highly interested clay mineral assemblage occurs in Sn-W ore spots enclosed in greisens [8] and in argillitized topaz-bearing granites. The Cínovec granite stock is relatively small, elliptical, vertical stratified body occurred in the central part of the Altenberg-Teplice caldera. The borehole CS-1, located in the center of granite stock, transacted lepidolite-bearing granite at the top of the section (about 90 m thick), an intermediate zone of zinnwaldite-bearing granite (thickness about 640 m) and a lower zone of protolithionite-bearing granite to the depth 1596 m. In uppermost part of granite stocks occurs irregular topaz-mica greisen bodies together with flat Sn-W ore veins enriched also in zinnwaldite and quartz. Clay minerals occur usually as filling of small cavities in quartz and/or as filling of small fissures accompanied flat ore veins [9].

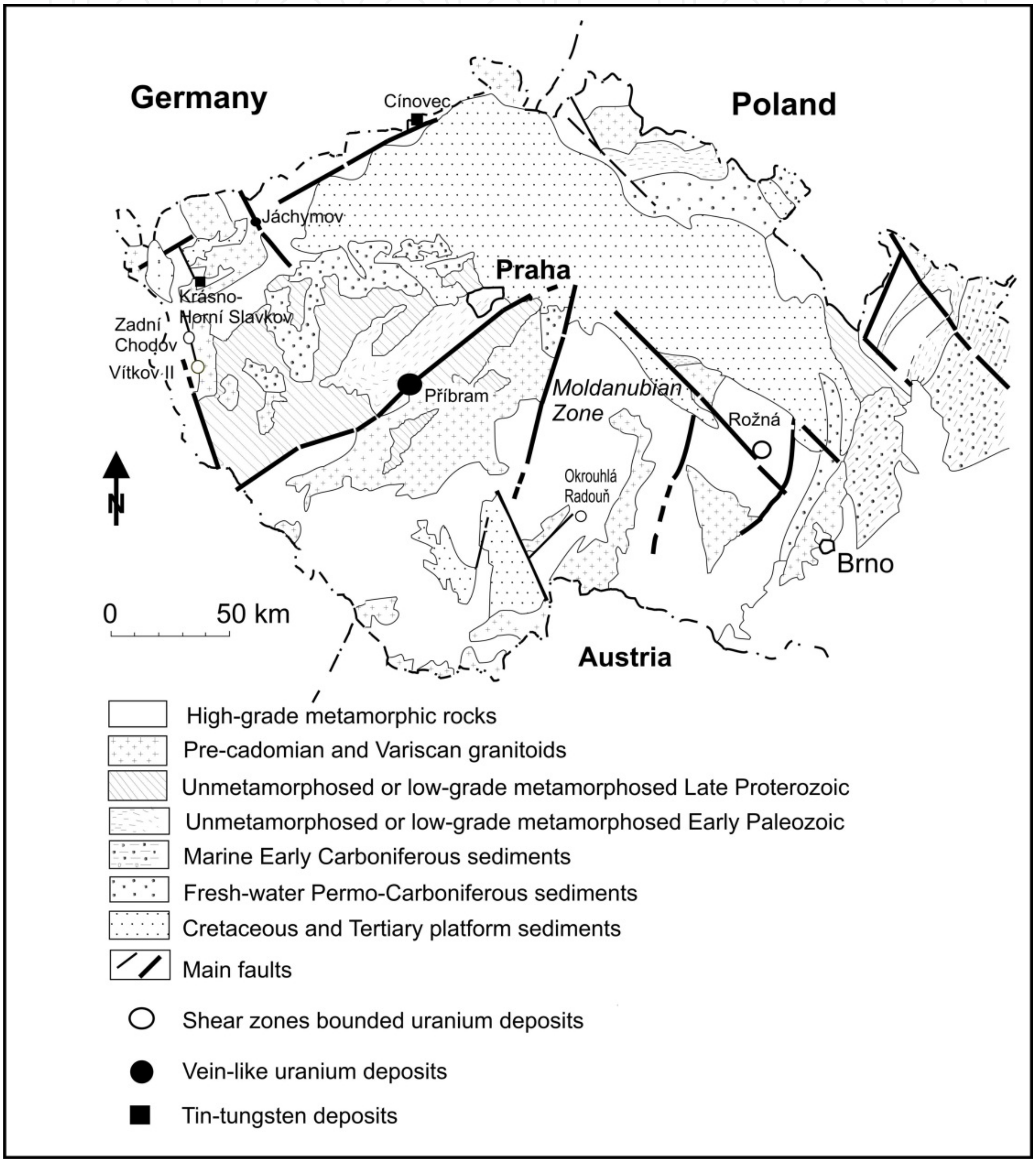

Figure 1. Geological sketch map of the Bohemian Massif.

Uranium ore deposits with a huge evolved argillization of country rocks occur in some shear zones of the Moldanubian Zone (Rožná–Olší ore district, Okrouhlá Radouň, Zadní Chodov, Vítkov II). The Moldanubian Zone represents a central, deeply eroded part of the Bohemian Massif. Therefore, in present-day section, it is composed dominantly of plutonic and high-grade metamorphic rocks (two-mica and biotite granites of the Moldanubian batholith, Třebíč pluton and Bor pluton).

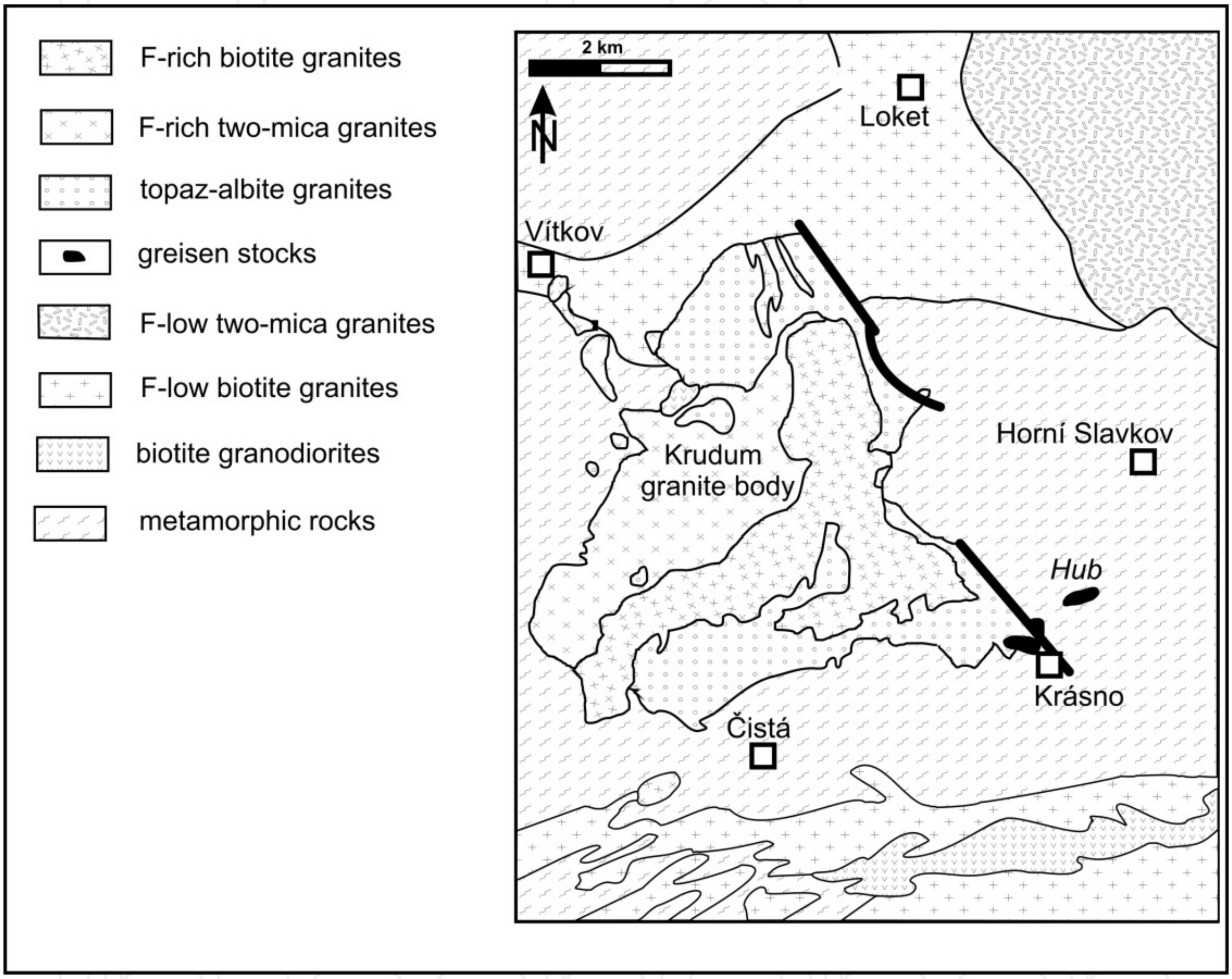

Figure 2. Geological sketch map of the Krásno–Horní Slavkov ore district.

The Rožná–Olší uranium district lies in the NE part of the Moldanubian Zone of the Bohemian Massif (Fig. 3). The high-grade metamorphic rocks of this zone were overthrust on its NE boundary by the Svratka Crystalline unit and on the easterly located Cadomian Brunovistulian foreland. The high-grade paragneisses of the Moldanubian Zone are subdivided into Monotonous, Varied and Gföhl Unit. The Rožná–Olší ore district is located in the uppermost Gföhl unit. The host rocks of the Rožná U-deposit consist mainly of biotite paragneisses and amphibolites with small bodies of calc-silicate rock, marble, serpentinite and pyroxenite. The subsequent exhumation of these rocks series to middle crustal levels was associated with kilometer-scale isoclinal folding. Longitudinal N–S to NNW–SSE striking ductile shear zones (Rožná and Olší shear zones) dip WSW at an angle of 70–90º

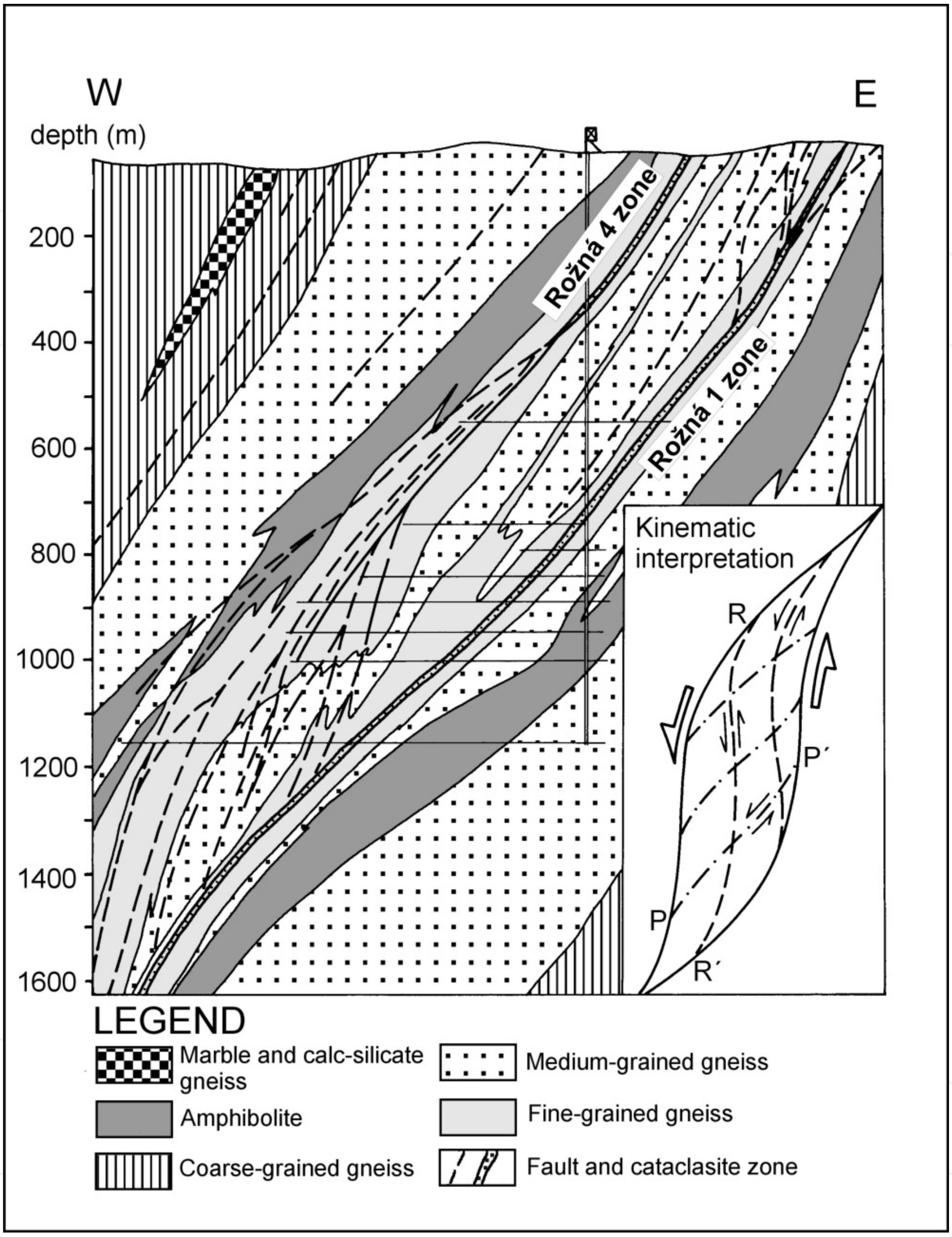

Figure 3. Cross section of the Rožná uranium deposit.

and strike parallel to the tectonic contact between the Gföhl unit and the Svratka Crystalline Unit. The main longitudinal faults of the Rožná shear zone are designated as Rožná 1 (R1) and Rožná 4 (R4) and host the main part of the disseminated uranium mineralization. The less strongly mineralized Rožná 2 (R2) and Rožná 3 (R3) fault zones host numerous separate pinnate carbonate veins. Longitudinal fault structures are crosscut and segment by steep, ductile to brittle NW–SE and SW–NE-striking fault zones that host post-uranium carbonate-quartz-sulfide mineralization. Uranium mineralization forms (i) disseminated coffinite>uraninite>U-Zr-silicate ore in chloritized, pyritized, carbonatized, and graphite-enriched cataclastites of longitudinal faults, (ii) uraninite>coffinite ore in carbonate veins, (iii) disseminated coffinite>uraninite in desilicified, albitized, and hematitized gneiss (episyenite) adjacent to longitudinal faults and (iiii) mostly coffinite ore bound to the intersection of the longitudinal structures. Total mine production of the Rožná-Olší ore district was 23,000 tons U with average grade of 0.24 % U. The Rožná uranium deposits is the last recently mined uranium deposit in Central Europe with annual production about 300 t U [10].

Okrouhlá Radouň uranium deposit is formed by NNW–SSE-striking shear zone occurred on the northeastern margin of the Klenov two-mica granite body in the southern part of the Bohemian Massif. Host-rock series of this ore deposit are formed by high-grade metasediments of the Moldanubian Varied group and peraluminous two-mica granites of the Moldanubian batholith. The shear zone is filled with cataclasites formed by host rocks, altered to clay minerals-rich and chlorite-rich assemblages with uranium mineralization enriched in coffinite, partly also in pitchblende [11, 12, 13]. Uranium ore deposits in the Bor pluton (Zadní Chodov, Vítkov II) are located in N-S to NW-SE shear zones evolved in biotite monzogranites of I/S-type [14, 15]. The hydrothermal alterations associated with uranium mineralization are represented particularly by the removal of quartz, chloritization, albitization, hematitization and origin of younger generations of chlorite and white mica (muscovite, phengite). Shear zones evolved on the west margin of the Bor pluton (Zadní Chodov), on the boundary between granites of the Bor pluton and metasediments of the Moldanubian Zone are distinctly enriched in more generation of chlorite accompanied by various clay minerals (smectite) [16].

3. Analytical methods

Clay minerals and chlorites were analyzed in polished thin sections using a CAMECA SX 100 electron microprobe working in WDX mode employing the PAP matrix correction program [17] at the Institute of Geology of the Academy of Sciences of the Czech Republic. The operating conditions were 15 kV acceleration voltage, 15 nA beam current, and 1–2 μm beam diameter. Counting times on the peaks were 10–30 seconds depending on the element. Background counts were measured in each case in half the time for peak measurement on both sides of the peak. Calibrations were done using standard sets from SPI. Standards included fluorite (F), jadeite (Na, Al), diopside (Ca), leucite (K), magnetite (Fe), quartz (Si), periclase (Mg), rhodonite (Mn), rutile (Ti), spinel (Cr) and tugtupite (Cl). Detection limits for these elements are as follows: F 0.09–0.15 wt%, other elements 0.03–0.20 wt%. Formulae of chlorite were calculated in relation to 36 (O, OH) atoms per formula unit (apfu), formulae of white mica and illite were calculated in relation to 24 (O, OH) apfu and formulae of clay minerals (kaolinite, smectite) were calculated on the basis of 18 (O, OH). For these calculations was used MINPET software. For calculation of chlorite thermometry was used a six-component chlorite solid solution model according Walshe (1986) [18].

Major elements in whole rock samples were determined by X-ray fluorescence spectrometry using the PANanalytical Axios Advanced spectrometer at Activation Laboratories Ltd., Ancaster, Canada. Trace elements were determined by ICP MS (a Perkin Elmer Sciex ELAN 6100 ICP mass spectrometer) at Activation Laboratories Ltd., Ancaster, Canada (Table 1). Whole rock samples enriched in clay minerals were used for sampling of clay mineral fractions. The size fraction of clay minerals in size below 4 μm was prepared by conventional sedimentation method. X-ray diffraction (XRD) analysis of clay minerals in clay-size fractions were obtained on untreated, ethylene-glycol solvated and heated samples using a Philips PW 7310 diffractometer with CuK_α radiation (40 kV, 40 mA) and Ni filter standard set.

4. Results

4.1. Petrology

The investigation of clay minerals assemblage occurred in Sn-W ore deposits of the Saxothuringian Zone (Bohemian Massif, Czech Republic) was concentrated on assemblages occurring in Sn-W ore pockets and highly argillized topaz-albite granites of the Hub stock (Krásno–Horní Slavkov ore district). The ore pockets are globular or even irregular bodies tens of centimetres in size, with a very high proportion of cassiterite, which are enclosed in topaz-mica greisens. Quartz, Li-micas, fine flakes of white mica (muscovite) and clay minerals (dickite, kaolinite, very rare cookeite) are the accompanying minerals of these ore pockets. Clay minerals matter filling small cavities between a bigger cassiterite grains has a grey appearance being a mixture of dickite, Li-, Al-chlorite (cookeite) with dickite and white mica. The identification of cookeite and illite was performed by X-ray diffraction method.

In highly argillized topaz-albite granites a complex clay minerals assemblage was identified using X-ray diffraction method and microprobe analysis. This very fine-grained assemblage enclosed between bigger grains of quartz, topaz and tables of Li-mica is formed of smectite, illite, kaolinite, dickite, chlorite and corrensite. Corrensite was identified on the basis of 29.2 Å XRD reflection on natural, oriented sample and 31.1 Å reflection after ethylene glycol treatment. These XRD reflections are significant for identification of corrensite [31]. In greisenized topaz-albite granites occurs sometimes also white mica (muscovite, hydromuscovite).

Disseminated uranium mineralization occurred in shear zones of the Rožná, Okrouhlá Radouň, Zadní Chodov and Vítkov uranium deposits comprises usually three stages (pre-ore, ore and post-ore stages). The first two stages are of the late-Variscan age; the last stage is very probably of the post-Variscan age. The pre-ore stage is characterized by a huge occurrence of inherited chlorite originated by chloritization of biotite (chlorite I). In syn-ore stage originated authigenic chlorite (chlorite II), together with authigenic Mg-Fe chlorite (chlorite III) occurred often as filling of small cavities in intensively altered paragneisses (Rožná, Okrouhlá Radouň, Zadní Chodov) and/or in altered granites (Okrouhlá Radouň, Vítkov II). During pre-ore stage originated also as relatively rare mineral white mica

wt%	Ko-55	R-1	R-2	Re-503	Re-510	OR-99	ZCH-6
SiO_2	75.52	51.85	45.76	57.42	53.81	49.42	44.30
TiO_2	0.03	1.30	0.98	0.62	0.08	0.30	0.33
Al_2O_3	13.23	18.36	15.37	18.76	18.35	15.47	9.45
Fe_2O_3 tot.	1.75	9.24	6.30	4.73	1.23	6.25	12.44
MnO	0.11	0.14	0.15	0.14	0.14	0.07	0.24
MgO	0.20	2.85	2.25	1.50	0.55	2.20	14.97
CaO	1.24	3.69	11.10	8.27	8.39	6.64	1.54
Na_2O	0.20	5.95	6.25	7.99	6.24	0.46	0.23
K_2O	1.65	1.89	0.97	0.55	1.10	1.38	0.01
P_2O_5	0.19	0.30	0.21	0.38	0.20	0.29	0.49
L.O.I.	5.40	4.41	9.52	0.33	9.32	17.55	15.81
Total	99.52	99.98	98.86	100.69	99.41	100.03	99.81
ppm							
U	16	877	833	232	353	436	4553
Th	3	4	6	20	7	8	21
Y	4	33	39	23	11	28	69
Zr	25	243	261	186	51	169	118
Ba	8	456	497	366	388	3	35
Rb	886	88	40	15	55	81	1
Sr	17	230	466	176	296	197	46
La	1.55	12.00	21.00	42.90	11.00	19.10	12.80
Ce	2.13	27.70	44.80	82.70	19.51	40.10	35.10
Pr	0.25	3.85	5.50	9.44	1.94	4.40	5.69
Nd	1.29	17.20	22.70	35.00	7.13	17.10	30.60
Sm	0.40	5.61	5.46	6.53	1.83	4.40	14.40
Eu	0.007	0.65	1.20	1.14	0.066	2.40	7.14
Gd	0.35	6.14	6.25	6.24	1.89	4.40	13.50
Tb	0.09	1.34	1.22	0.83	0.34	0.82	2.72
Dy	0.61	9.13	7.26	4.85	2.45	5.40	15.30
Ho	0.09	1.86	1.47	0.86	0.48	1.10	2.74
Er	0.27	6.10	4.06	2.54	1.45	2.40	7.45
Tm	0.06	0.99	0.67	0.38	0.20	0.44	1.11
Yb	0.36	6.68	4.22	2.25	1.49	3.20	6.90
Lu	0.04	1.03	0.60	0.31	0.22	0.46	0.86
ΣREE	7.50	100.29	126.41	195.97	50.00	105.72	156.31
La_N/Yb_N	2.91	1.21	..3.36	12.88	4.96	4.03	1.25
Eu/Eu*	0.06	0.34	0.63	0.55	0.11	1.67	1.56
Th/U	0.188	0.005	0.007	0.087	0.020	0.018	0.005

Table 1. Representative analyses of altered rocks from the Sn-W and U ore deposits of the Bohemian Massif.

Ko-55 – argillized topaz-albite granite, Hub stock, Krásno–Horní Slavkov ore district, R-1, R-2 – altered biotite gneiss, Rožná uranium deposit, Re-503 – altered biotite gneiss, Okrouhlá Radouň uranium deposit, Re-510 – altered two-mica granite, Okrouhlá Radouň uranium deposit, OR-99 – altered biotite gneiss, Okrouhlá Radouň uranium deposit, ZCH-6 altered biotite gneiss, Zadní Chodov uranium deposit. REE – rare earth elements, La_N/Yb_N = LREE/HREE (light rare earth elements/heavy rare earth elements, $Eu/Eu^* = Eu_N/\sqrt{(Sm_N \times Gd_N)}$. Normalising values of chondrites are from Taylor and McLennan [29].

(muscovite, hydromuscovite, phengite). For syn-ore stage is origin of various clay minerals (Fe-illite, smectite, kaolinite) significant. Compared with voluminous pre-ore and syn-ore stage alteration, post-ore stage alteration is usually restricted to origin of small authigenic chlorite-carbonate veins and/or veilets and disseminations of chlorite in carbonatized host rocks (chlorite IV). The origin of the youngest chlorite is sometimes accompanied by origin of clay minerals (illite, kaolinite).

5. Geochemistry of altered rocks

The chemical composition of arigillized topaz-albite granites connected with Sn-W mineralization was investigated in area of the Hub stock (Krásno–Horní Slavkov ore district). Argillitized granites are in comparison with original topaz-albite granite enriched in CaO and MgO and depleted in alkalies (Fig. 4). During argillization of topaz-albite granites were also accessory minerals (monazite and zircon) partly dissoluted and argillized granites were depleted in REE (Fig. 5).

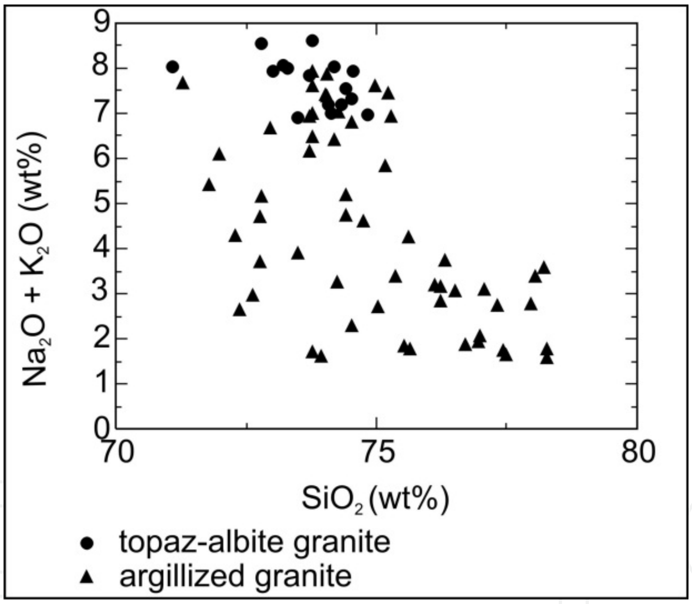

Figure 4. Plot of $Na_2O + K_2O$ (wt%) vs. SiO_2 (wt%) for arigillized granites from the Krásno–Horní Slavkov ore district.

Geochemistry of altered high-grade metamorphic rocks was studied in the area of the Rožná, Okrouhlá Radouň and Zadní Chodov uranium ore deposits. The distribution of REE in barren, pre-ore altered (desilicified, albitized, hematitized and chloritized) biotite paragneisses of all three examined uranium deposits usually display patterns similar to those of the parent paragneisses. Barren, syn-ore argillized, chloritized and in the Okrouhlá Radouň uranium deposit also strongly carbonatized rocks show significantly lower bulk contents of REE (49–232 ppm) and relatively high LREE/HREE ratios (8.7–17.6) in comparison with hydrothermally unaffected gneisses. Higher LREE/HREE ratio (12.8–16.1), i.e. high depletion on HREE was found in graphitised cataclastites from the Rožná uranium deposit, which are characterized by the lowest bulk content of REE (49–98 ppm) (Fig. 6).

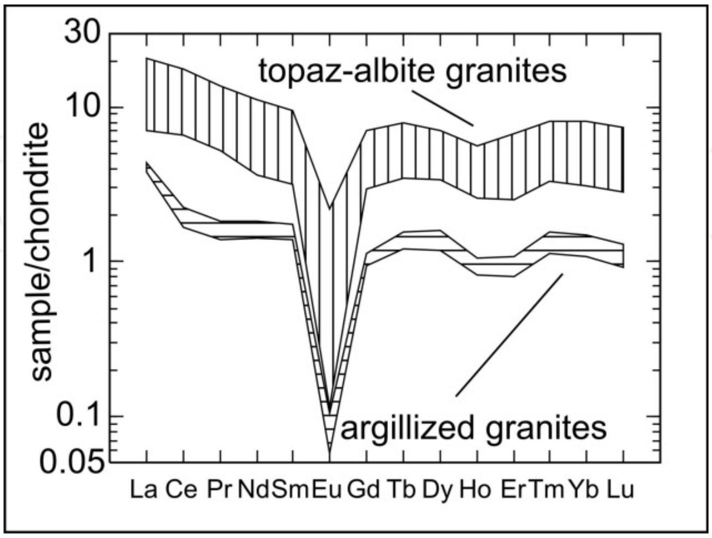

Figure 5. Chondrite normalized REE patterns for topaz-albite granites and argillized granites from the Krásno–Horní Slavkov ore district. Normalising values are from Taylor and McLennan [29].

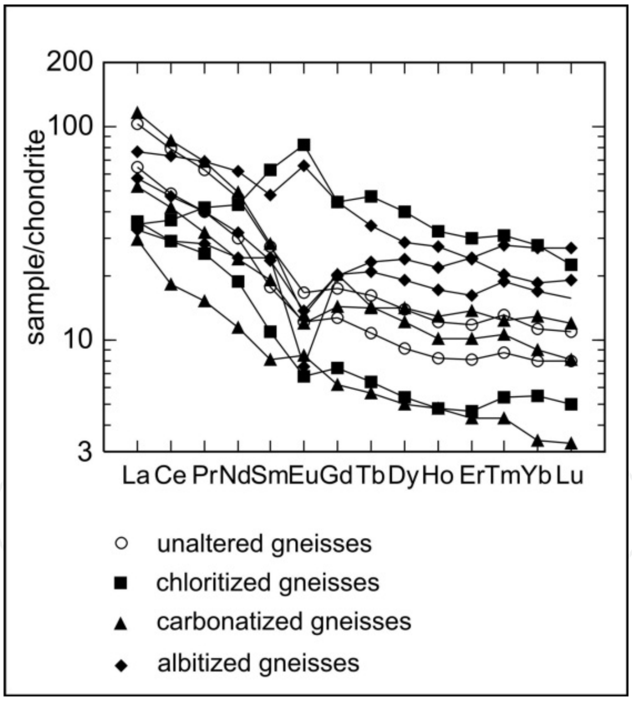

Figure 6. Chondrite normalized REE patters for hydrothermally altered rocks from the Rožná and Okrouhlá Radouň uranium deposits. Normalising values are from Taylor and McLennan [29].

The geochemistry of altered granites connected with uranium mineralization was studied in the Okrouhlá Radouň and Vítkov II uranium deposits. Hydrothermal alteration of two-mica granites from the southern part of the Okrouhlá Radouň uranium deposit is characterized by a higher Fe_2O_3/FeO ratio and by a significant depletion in SiO_2 contents. Highly altered granites typically show high contents of Na_2O and usually low contents of K_2O. The content of K_2O is higher only at the presence of higher amounts of newly originated white mica (muscovite) and/or illite. The later carbonatization of quartz-depleted altered granites is characterized by high contents of CaO and CO_2. The hydrothermal alteration of granites is, due to the dissolution of K-feldspar, connected with a depletion in Rb and sometimes also with the evolution of a prominent negative europium anomaly (Eu/Eu* = 0.11). The higher content of HREE in altered granites is connected with the origin of uranium mineralization and a higher concentration of HREE in coffinite. Chloritization of porphyric biotite granite from the Bor pluton at the Vítkov II uranium deposit are accompanied by the silica removal, which continued during the argillization. A moderate increase in TiO_2 and P_2O_5 contents occurred in the course of the hydrothermal alterations. Contents of $A1_2O_3$ and Fe_2O_3 increased during the chloritization and argillization. In the course of chloritization, the content of FeO and MgO increased considerably, which is reflected by the formation of chlorites I richer in iron. The MgO content also increased sizeably during argillization. The content of CaO increases in the granites affected by carbonatization and it decreases in the rocks affected by chloritization and in majority of argillized granites. The content of Na_2O increases in the rocks affected by albitization, it is considerably lower in the argillized granites.

6. Composition of chlorite

In altered paragneisses and granites of above-mentioned uranium ore deposits chlorite occurs usually in four generations (chlorite I, II, III, IV). The main portions of chlorite are formed by inherited chlorite I and inherited to authigenic chlorite II, which occurs in shear zones. These shear zones host the main part of the disseminated uranium mineralization. The chlorite I often preserves the morphology of original biotite, whereas chlorite II forms fluidal aggregates in cataclastites, represented the predominant filling of shear zones. The both later chlorite generations (chlorite III and IV) crystallized in free voids of rocks originated due to quartz dissolution. The composition of these four chlorite generations in individual uranium deposits is quite different. The inherited chlorite of pre-ore and syn-ore stage is pycnochlorite to brunsvigite (Fig. 7, 8, 9).

In the Rožná uranium deposit occurs also Mg-rich inherited to authigenic chlorite (diabantite), which forms fluidal aggregates in shear zones (matrix chlorite). For inherited chlorite from the Rožná uranium deposit is significant relatively high content of Si (up to 7.21 apfu). The content of Si in inherited chlorite from pre-ore stage of the Okrouhlá Radouň, Zadní Chodov and Vítkov II uranium deposits is distinctly lower (4.38–6.44) (Fig. 8, 9). Likewise occur differences in Mg/(Mg + Fe) ratio. Distinctly Fe-enriched inherited chlorites (brunsvigite) occur in shear zones of the Rožná and Okrouhlá Radouň uranium deposits with Mg/(Mg + Fe) ratio from 0.13 to 0.43. However, the inherited to authigenic chlorite from the Rožná uranium deposit is Mg-enriched chlorite (diabantite) with Mg/(Mg + Fe) ratio from 0.48 to 0.69 (Fig. 7).

The authigenic chlorites from all these uranium deposits are in comparison with inherited chlorites enriched in Mg. The lower enrichment in Mg displays the authigenic chlorites from the Rožná and Okrouhlá Radouň uranium deposits, whereas high enrichment in Mg

wt.%	Ro-5	Ro-16	Ro-27	Ra-13	Ra-54	ZCH-1	Vi-18
SiO_2	29.81	30.36	31.91	27.47	25.09	27.28	26.03
TiO_2	0.36	0.00	1.74	0.04	0.12	0.00	0.11
Al_2O_3	14.34	16.32	13.97	20.85	20.60	20.40	20.41
Cr_2O_3	0.02	0.00	0.00	0.01	0.02	0.05	0.00
FeO	33.66	26.75	17.70	22.49	32.95	20.73	25.99
MnO	0.42	0.27	0.31	0.19	0.21	0.15	0.37
MgO	8.77	13.92	19.54	16.40	9.48	19.09	13.95
CaO	0.28	0.27	0.00	0.14	0.04	0.00	0.07
Na_2O	0.62	0.00	0.60	0.06	0.00	0.06	0.20
K_2O	0.10	0.00	1.31	0.07	0.02	0.04	0.09
F	0.00	0.00	0.00	0.11	0.00	0.00	0.00
Cl	0.00	0.00	0.00	0.00	0.01	0.00	0.00
H_2O calc.	10.97	11.41	11.72	11.56	11.03	11.71	11.26
O=(F, Cl)	0.00	0.00	0.00	0.05	0.00	0.00	0.00
Total	99.35	99.32	98.80	99.34	99.57	99.51	98.48
apfu							
Si^{4+}	6.52	6.38	6.53	5.67	5.46	5.59	5.54
Al^{IV}	1.48	1.62	1.47	2.33	2.54	2.41	2.46
Al^{VI}	2.21	2.42	1.90	2.75	2.73	2.51	2.26
Ti^{4+}	0.06	0.00	0.27	0.01	0.02	0.00	0.02
Fe^{2+}	6.15	4.70	3.03	3.89	5.99	3.55	4.63
Cr^{2+}	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Mn^{2+}	0.08	0.05	0.05	0.03	0.04	0.03	0.07
Mg^{2+}	2.86	4.36	5.96	5.05	3.07	5.83	4.43
Ca^{2+}	0.07	0.06	0.00	0.03	0.01	0.00	0.02
Na^{1+}	0.26	0.00	0.24	0.02	0.00	0.02	0.08
K^{1+}	0.03	0.00	0.34	0.02	0.01	0.01	0.02
F^{1-}	0.00	0.00	0.00	0.14	0.00	0.00	0.00
Cl^{1-}	0.00	0.00	0.00	0.00	0.01	0.00	0.00
OH^{1-}	16	16	16	15.92	16	16	16
O	36	36	36	36	36	36	36
Mg/(Mg + Fe)	0.32	0.48	0.66	0.57	0.34	0.62	0.49

Table 2. Representative analyses of chlorites from the Rožná, Okrouhlá Radouň, Zadní Chodov and Vítkov II uranium deposits.

Ro-5 – inherited chlorite, ore stage, Rožná, Ro-16 –authigenic chlorite, post-ore stage, Rožná, Ro-27 – inherited to authigenic chlorite, pre-ore stage, Rožná, Ra-13 – authigenic chlorite, ore stage, Okrouhlá Radouň, Ra-54 –inherited chlorite, pre-ore stage, Okrouhlá Radouň, ZCH-1 – inherited chlorite, pre-ore stage, Zadní Chodov, Vi-18 –inherited chlorite, pre-ore stage, Vítkov II.

displays chlorites from the West Bohemian uranium deposits (Zadní Chodov, Vítkov II) (Fig. 7, 8, 9). The Mg/(Mg + Fe) ratio for authigenic chlorite from syn-ore and post-ore stage of the Rožná uranium deposit is quite similar (0.45–0.55), whereas the values of this ratio for authigenic chlorite from the Okrouhlá Radouň uranium deposit are partly lower (0.30–0.57). However, the Mg/(Mg + Fe) ratio in authigenic chlorites from the Zadní Chodov and Vítkov II uranium deposits is distinctly higher (0.74–0.88).

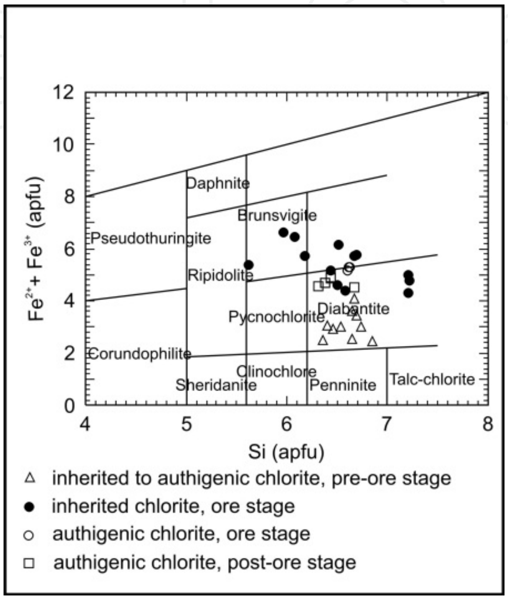

Figure 7. Classification diagram for chlorite from the Rožná uranium deposit according Hey [30].

From chemical composition of chlorites can be estimated temperatures of hydrothermal alterations in these ore deposits. The used chlorite thermometer for chlorites from pre-ore stage in the Rožná uranium deposit yielded temperatures from 219 ºC to 310 ºC. Authigenic syn-ore chlorites from all four uranium deposits indicate a temperature range from 145 ºC to 210 ºC. Authigenic post-ore chlorites are relatively rare and yielded temperatures for 150 ºC to 170 ºC.

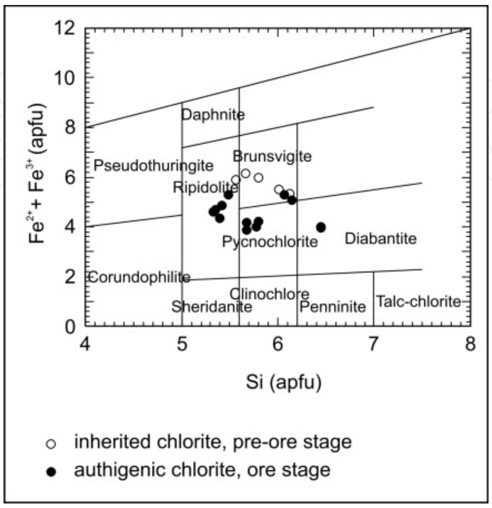

Figure 8. Classification diagram for chlorite from the Okrouhlá Radouň uranium deposit according Hey [30].

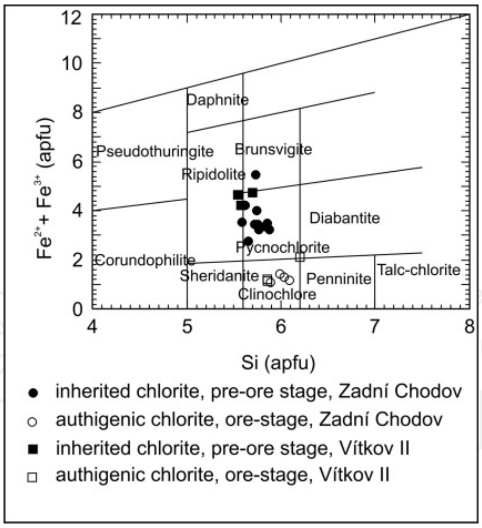

Figure 9. Classification diagram for chlorite from the Zadní Chodov and Vítkov II uranium deposits according Hey [30].

7. Composition of white mica

The white mica occurs in altered rocks of the Sn-W and U ore deposits as relatively rare mineral. The majority of white mica has composition of muscovite with variable content of water (hydromuscovite), Fe, Mg, Na and Ca (Table 3, Fig. 10).

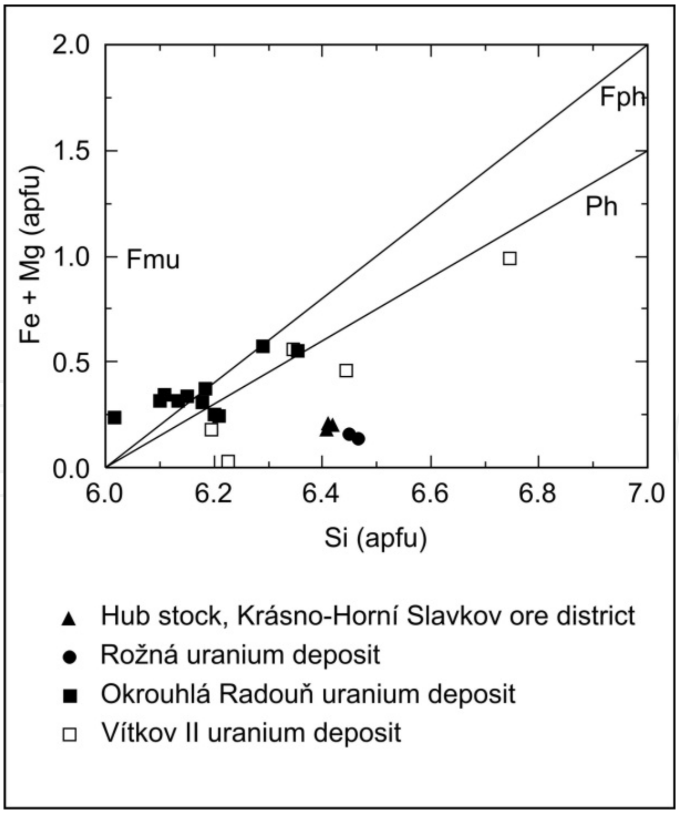

Figure 10. Plot of Fe + Mg (apfu) vs. Si (apfu) for white mica from the Krásno–Horní Slavkov ore district, Rožná, Okrouhlá Radouň and Vítkov II uranium deposits.

wt.%	Hub-27	Hub-30	Ro-12	Ra-1	Ra-2	Vi-1	Vi-3	Hub-18	Hub-19	SPO-2
SiO_2	48.30	48.87	48.82	46.63	45.45	45.96	47.98	50.90	50.94	48.52
TiO_2	0.06	0.05	0.00	0.12	0.02	0.32	0.40	0.03	0.01	0.08
Al_2O_3	34.38	34.69	34.37	35.52	37.23	34.07	33.25	34.83	35.52	26.03
Cr_2O_3	0.01	0.01	0.00	0.05	0.02	0.00	0.00	0.03	0.00	0.00
FeO	1.41	1.28	0.24	1.48	1.06	0.64	1.05	0.98	1.42	6.82
MnO	0.04	0.06	0.00	0.02	0.08	0.02	0.00	0.19	0.16	0.04
MgO	0.27	0.30	0.56	0.73	0.62	0.54	2.25	0.19	0.28	1.78
CaO	0.05	0.05	0.00	0.01	0.00	2.62	0.00	0.29	0.46	0.15
Na_2O	0.16	0.19	0.40	0.69	0.67	0.02	0.26	0.12	0.15	0.06
K_2O	10.10	10.21	9.69	10.55	10.78	10.07	10.21	8.32	7.13	9.31
F	0.91	0.90	0.00	0.08	0.03	0.00	0.00	0.31	0.15	0.00
Cl	0.01	0.02	0.00	0.01	0.00	0.00	0.00	0.00	0.03	0.00
H_2O calc.	4.08	4.13	4.53	4.49	4.52	4.45	4.53	4.50	4.60	4.30
Total	99.78	100.76	98.61	100.38	100.48	98.71	99.93	100.69	100.85	97.09
apfu										
Si^{4+}	6.41	6.42	6.47	6.18	6.02	6.19	6.35	6.57	6.53	6.77
Al^{IV}	1.59	1.58	1.53	1.82	1.98	1.81	1.66	1.43	1.47	1.23
Al^{VI}	3.78	3.79	3.83	3.72	3.82	3.60	3.52	3.86	3.89	3.04
Ti^{4+}	0.01	0.01	0.00	0.01	0.00	0.03	0.04	0.00	0.00	0.01
Fe^{2+}	0.16	0.14	0.03	0.16	0.12	0.07	0.12	0.11	0.15	0.80
Cr^{2+}	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
Mn^{2+}	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.02	0.02	0.01
Mg^{2+}	0.05	0.06	0.11	0.14	0.12	0.11	0.44	0.04	0.05	0.37
Ca^{2+}	0.01	0.01	0.00	0.00	0.00	0.38	0.00	0.04	0.06	0.02
Na^{1+}	0.04	0.05	0.10	0.18	0.17	0.01	0.07	0.03	0.04	0.02
K^{1+}	1.71	1.71	1.64	1.78	1.82	1.73	1.72	1.37	1.17	1.66
OH^{1-}	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
O	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00	24.00
Mg/(Mg + Fe)	0.25	0.30	0.80	0.47	0.51	0.60	0.79	0.26	0.26	0.32

Table 3. Representative analyses of white mica and illite from the Krásno—Horní Slavkov ore district, Rožná, Okrouhlá Radouň and Vítkov II uranium deposits.
Hub-27, 30 – muscovite, argillized granite, Krásno–Horní Slavkov ore district, Ro-12 – muscovite, altered gneiss, Rožná uranium deposit, Ra-1, 2 – muscovite, altered two-mica granite, Okrouhlá Radouň uranium deposit, Vi-1, 3 – muscovite, altered biotite granite, Vítkov II uranium deposit, Hub-18, 19 – illite, argillized granite, Krásno–Horní Slavkov ore district, SPO-2 – illite, altered gneiss, Rožná uranium deposit.

The lowest content of Fe (0.01–0.16 apfu), Mg (0.00–0.06 apfu), Na (0.01–0.05 apfu) and Ca (0.00–0.01 apfu) displays muscovite from greisenized topaz-albite granites of the Hub stock (Krásno–Horní Slavkov ore district). Similar low contents of these elements were found in white mica from the Rožná uranium deposit. The white mica from the Okrouhlá Radouň uranium deposit is partly enriched in Fe (up to 0.43 apfu) and Mg (0.11–0.39 apfu). The white mica from this uranium deposit displays also enrichment in Na (0.12–0.22 apfu). The white mica from the Vítkov II uranium deposit has highly variable content of Mg (0.0–0.73 apfu) and analysis with the highest content of Mg can be classified as phengite (Fig. 10).

8. Composition of clay minerals

Chemical composition of clay minerals (illite, kaolinite, smectite, corrensite) was determined only for illite, kaolinite and smectite. Corrensite is distinctly rare mineral, which was not found in thin sections that are analysed by microprobe. Kaolinite and illite were identified by XRD method in all examined deposits. Chemical analyses of these clay minerals were plotted in the $M^+R^3 - 2R^3 - 3R^2$ diagram modified by Velde [19] (Table 4, Fig. 11). However, they are analysed only in argillized granites from the Krásno–Horní Slavkov ore district and in altered rocks from the Rožná and Okrouhlá Radouň uranium deposits. In kaolinite from argillized granites of the Hub stock (Krásno–Horní Slavkov ore district) content of Si is lower (3.45–4.08 apfu) than its content in kaolinite from altered rocks in the Okrouhlá Radouň uranium deposit (4.03–4.17 apfu). Some differences in chemical composition of kaolinite from both ore deposits display also contents of Fe, Mg, Ca and K. In kaolinite from the Krásno–Horní Slavkov Sn-W ore district occur enrichment in Fe (0.02–0.26 apfu), Ca (0.00–0.07 apfu) and K (0.00–0.10 apfu). Contents all these elements in kaolinite from the Okrouhlá Radouň uranium deposit are lower – Fe (0.01–0.08 apfu), Ca (0.01–0.06 apfu) and

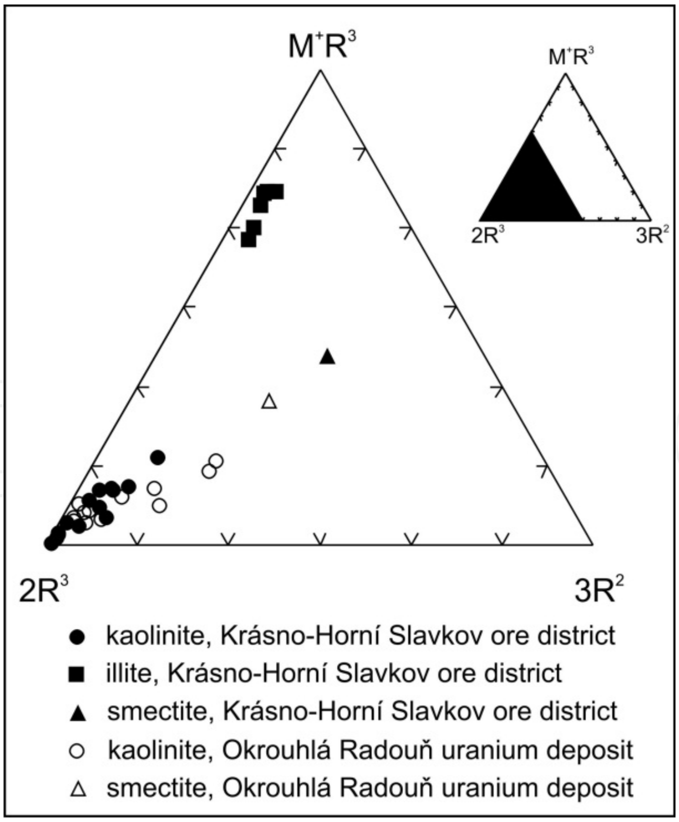

Figure 11. Plot of $M^+R^3 - 2R^3 - 3R^2$ according Velde [19] for clay minerals from the Krásno–Horní Slavkov ore district and Okrouhlá Radouň uranium deposit.

wt.%	Hub-13	Hub-30	Hub-36	Ra-12	Ra-15	Ra-16	Ra-13
SiO_2	46.80	46.92	39.52	48.38	50.57	47.27	52.05
TiO_2	0.00	0.02	0.00	0.02	0.00	0.00	0.00
Al_2O_3	38.61	38.01	14.06	36.66	30.43	37.32	27.18
Cr_2O_3	0.01	0.00	0.00	0.00	0.00	0.01	0.02
FeO	0.30	0.23	1.43	0.31	1.10	0.11	1.49
MnO	0.00	0.06	0.11	0.00	0.02	0.06	0.00
MgO	0.07	0.08	0.06	0.46	3.06	0.28	3.49
CaO	0.15	0.08	0.08	0.21	0.58	0.46	0.64
Na_2O	0.04	0.05	0.02	0.02	0.01	0.01	0.06
K_2O	0.20	0.06	0.36	0.03	0.47	0.01	1.85
F	0.09	0.08	0.00	0.00	0.00	0.00	0.00
Cl	0.00	0.01	0.00	0.01	0.03	0.00	0.05
H_2O calc.	13.88	13.80	13.74	13.96	13.82	13.85	13.74
O=(F, Cl)	0.04	0.04	0.00	0.00	0.01	0.00	0.01
Total	100.11	99.36	100.38	100.36	100.08	99.49	100.56
apfu							
Si^{4+}	4.03	4.06	3.45	4.16	4.39	4.09	4.54
Al^{IV}	0.00	0.00	0.55	0.00	0.00	0.00	0.00
Al^{VI}	3.92	3.88	4.08	3.71	3.11	3.81	2.79
Ti^{4+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe^{2+}	0.02	0.02	0.10	0.02	0.08	0.01	0.11
Cr^{2+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn^{2+}	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Mg^{2+}	0.01	0.01	0.01	0.06	0.40	0.04	0.45
Ca^{2+}	0.01	0.01	0.01	0.02	0.05	0.04	0.06
Na^{1+}	0.01	0.01	0.00	0.00	0.00	0.00	0.01
K^{1+}	0.02	0.01	0.04	0.04	0.05	0.01	0.21
F^{1-}	0.05	0.04	0.00	0.00	0.00	0.00	0.00
Cl^{1-}	0.00	0.00	0.00	0.00	0.01	0.00	0.02
OH^{1-}	7.98	7.98	8.00	8.00	8.00	8.00	7.99
O	18.00	18.00	18.00	18.00	18.00	18.00	18.00
Mg/(Mg + Fe)	0.29	0.37	0.07	0.73	0.83	0.82	0.81

Table 4. Representative analyses of clay minerals from the Krásno–Horní Slavkov ore district and Okrouhlá Radouň uranium deposit.
Hub-13, 30, 36 – kaolinite, argillized granite, Krásno–Horní Slavkov ore district, Ra-12, 15, 16 – kaolinite, argillized gneiss, Okrouhlá Radouň uranium deposit, Ra-13 – smectite, argillized gneiss, Okrouhlá Radouň uranium deposit.

K (0.00–0.08 apfu). However, the content of Mg (0.02–0.45 apfu) is partly higher in kaolinite from the Okrouhlá Radouň ore deposit, whereas kaolinite from the Krásno–Horní Slavkov ore district is in Mg depleted (0.00–0.07 apfu). Illite from both type deposits is partly enriched in Fe (0.07–0.11 apfu). Smectite from the Krásno–Horní Slavkov ore district is enriched in Fe (0.25 apfu) and Ca (0.15 apfu), whereas smectite from the Okrouhlá Radouň ore deposit is enriched in Mg (0.45 apfu).

9. Discussion

The associations of chlorites and clay minerals and their chemistry were studied in unconformity-type uranium deposits occurred in Canada [6] and Australia [1, 2]. In these deposits were studied layered silicates in mineralized shear zones, which are evolved in various altered metasediments. In both areas are clay minerals represented predominantly by chlorites and smectites. Authigenic chlorites from unconformity-type uranium deposits occurred in Australia are enriched in Mg [1,2]. The clay minerals assemblage is usually enriched in illite-smectite mixed layer minerals. Illite-smectite mixed layer minerals together with kaolinite and chlorite are characteristic for argillized granitic rocks occurred in uranium ore deposits from the French Massif Central [3]. The temperatures, which were determined by chlorite thermometry in the Rožná, Okrouhlá Radouň and Vítkov II uranium deposits can be well correlated with temperatures obtained by study of fluid inclusions [10, 20].

The greisenized and argillized granites connected with Sn-W mineralization are usually enriched in kaolinite and illite [4, 5, 7]. In greisens from Sn-W ore deposits evolved in the Saxothuringian Zone of the Bohemian Massif was also found dickite [9], together with smectite and illite-smectite mixed layer minerals [21]. The cookeite, which was found in cassiterite–enriched pockets in the Krásno–Horní Slavkov ore district [8] occurs also in other tin ore deposits [22]. Temperature of the cookeite origin can be estimated from data on cookeite stability [23] at 270–350 ^{o}C. This temperature can be well correlated with temperatures of clay minerals origin in ore pockets obtained by fluid inclusion study [24]. Occurrences of corrensite were recorded usually from hydrothermally altered intermediate to basic volcanic rocks [25, 26, 27]. Similar association of corrensite with kaolinite, illite and mixed-layer illite/smectite was found in granitic cupola of the Montebras, France [28]. According to Velde [19], the thermal stability of corrensite ranges from 180–200 ^{o}C to 280 ^{o}C. This temperature is in agree with the homogenization temperatures, which were found in quartz-fluorite veinlets occurred in arigilized greisens of the Krásno–Horní Slavkov ore district [24].

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