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Perovskite from Ca-Mg skarn-porphyry deposit Vysoká – Zlatno, Štiavnica stratovolcano, Slovakia

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Abstract

Disseminated euhedral to subhedral crystals of perovskite (up to 200 μm across) occur in association with monticellite, clintonite, magnetite, spinel, andradite, hydroxylellestadite, calcite and anhydrite in Ca-Mg skarn at the contact between Miocene granodiorite porphyry intrusion and the Middle Triassic dolomites in a borehole from the Cu-Au skarn-porphyry deposit Vysoká – Zlatno near Banská Štiavnica (Štiavnické vrchy Mts., Central Slovakia). Perovskite crystals show the near end-member compositions: 94 to 98 mol.% of $CaTiO_3$; they reveal domains enriched in Fe, REE´s, and Th (up to 2.8 wt.% Fe_2O_3, ≤6 wt.% $(La+Ce+Nd)_2O_3$, ≤5.5 wt.% ThO_2). Contents of U, Zr, Hf, Nb, Ta, Sr, and Na are relatively low (≤0.01 *apfu*). The compositional variations indicate a limited range of $REE^{3+}Fe^{3+}Ca_{-1}Ti_{-1}$ substitutions. Perovskite originated during the prograde, peak-metamorphic conditions of high-temperature contact thermal metamorphism related to emplacement of the granodiorite porphyry into dolomites. Irregular domains in some perovskite crystals indicate a partial redistribution of REE´s, Fe and other elements during younger hydrothermal (?) process, possibly connected with the fluid-driven retrograde stage of the skarn evolution.

Key words: perovskite, electron microprobe, skarn, skarn-porphyry deposit, Štiavnica stratovolcano, Vysoká – Zlatno, Slovakia

Introduction

Perovskite ($CaTiO_3$) represents a typical accessory mineral in (ultra)mafic and alkaline magmatic rocks, such as alkali basalts, pyroxenites, melilitites, ijolites, nepheline syenites, alkaline pegmatites, kimberlites, carbonatites (e.g., Mitchell, 1972; Jones and Wyllie, 1984; Ulrych et al., 1988, 1996, 2005, 2008; Deer et al., 1995; Anthony et al., 1997; Mitchell and Chakhmouradian, 1998). It occurs in Ca, Al-rich inclusions in some carbonaceous chondritic meteorites, as well as in metamorphic rocks, mainly contact-metamorphosed impure limestones and calcareous skarns, chlorite schists and altered serpentinites (e.g., Deer et al., 1995; Anthony et al., 1997; Marincea et al., 2001; Rosa and Martin, 2010). Perovskite is orthorombic (pseudocubic) mineral with extremely densely packed structure. Therefore, a perovskite-structure silicate phase $(Mg,Fe)SiO_3$ is probably an important constituent of the Earth´s lower mantle in association with Mg-rich wüstite, in depths of 400 to 1 000 km (e.g., Deer et al., 1995).

Our contribution describes accessory perovskite, including compositional variations of the main and trace elements, from Ca-Mg skarn in an exocontact of granodiorite porphyry intrusion associated with subeconomic Cu-Au skarn-porphyry deposit Vysoká – Zlatno, hosted by the Štiavnica stratovolcano in the Central Slovakia.

Geological setting and mineral assemblages of skarns at Vysoká – Zlatno

The Vysoká – Zlatno Cu-Au skarn-porphyry deposit is situated between Hodruša-Hámre and Uhliská villages in the western part of the central zone of the Štiavnica stratovolcano, located in the Central Slovakian Neogene Volcanic Field. Major mineralization overlaps with the zone of skarns at contacts between the biotite-amphibole granodiorite porphyry stock and the Triassic carbonates of the Veľký Bok Group (Fig. 1). The skarn mineralization is of Mg-Ca type, developed both in altered dolomites and limestones (exoskarns) and on the margins of the porphyry intrusion (endoskarns) in depth of ca 670 to 1 000 m.

The skarn rocks are variably represented by the prograde and retrograde Mg- and Ca-skarn mineral assemblages, described in detail by Zábranský (1976), Kúšik (1992), Marsina et al. (1995) and Koděra et al. (2009). Prograde stage minerals include forsterite, wollastonite, diopside, garnet (grossular to andradite), monticellite, spinel, magnetite, and ilmenite. The retro-

grade mineral assemblage could be subdivided into (1) older, higher-temperature substage with phlogopite and chlorite, accompanied by actinolite to tremolite, clintonite, epidote, titanite and vesuvianite, and (2) younger, lower-temperature substage with talc, serpentinite, brucite, hydroxylellestadite, anhydrite and carbonates with magnetite, hematite, sulphide minerals (pyrrhotite, pyrite, chalcopyrite, sphalerite, molybdenite) and rare gold.

In our study, the perovskite and associated minerals has been studied in a sample of Mg-Ca skarn from the R-1 borehole material, depth of 677 m, located on the northern margin of the deposit.

Analytical methods

Perovskite in polished section was analysed with the Cameca SX 100 electron microprobe using the wave-dispersion mode (WDS) and imaged by back-scattered electrons (BSE) at the Slovak Geological Survey, Bratislava. The following analytical conditions were applied: 15 kV accelerating voltage, 20 nA beam current, and 2 to 3 μm beam diameter. Used standards and lines included ferrocolumbite (Nb Lα), manganotantalite (Ta Mα), orthoclase (Si Kα), TiO_2 (Ti Kα), $ZrSiO_4$ (Zr Lα), SnO_2 (Sn Lα), ThO_2 (Th Mα), UO_2 (U Mβ), Al_2O_3 (Al Kα), YPO_4 (Y Lα), $LaPO_4$ (La Lα), $CePO_4$ (Ce Lα), $PrPO_4$ (Pr Lβ), $NdPO_4$ (Nd Lα), $SmPO_4$ (Sm Lα), $EuPO_4$ (Eu Lβ), $GdPO_4$ (Gd Lα), $TbPO_4$ (Tb Lα), $DyPO_4$ (Dy Lα), $HoPO_4$ (Ho Lβ), $ErPO_4$ (Er Lβ), $TmPO_4$ (Tm Lα), $YbPO_4$ (Yb Lα), $LuPO_4$ (Lu Lβ), fayalite (Fe Kα), rhodonite (Mn Kα), forsterite (Mg Kα), wollastonite (Ca Kα), $PbCO_3$ (Pb Mα), albite (Na Kα), and LiF (F Kα). Counting times of 20 to 40 seconds were used for the measured elements. The detection limits of measured elements range from 0.02 to 0.1 wt.%, and

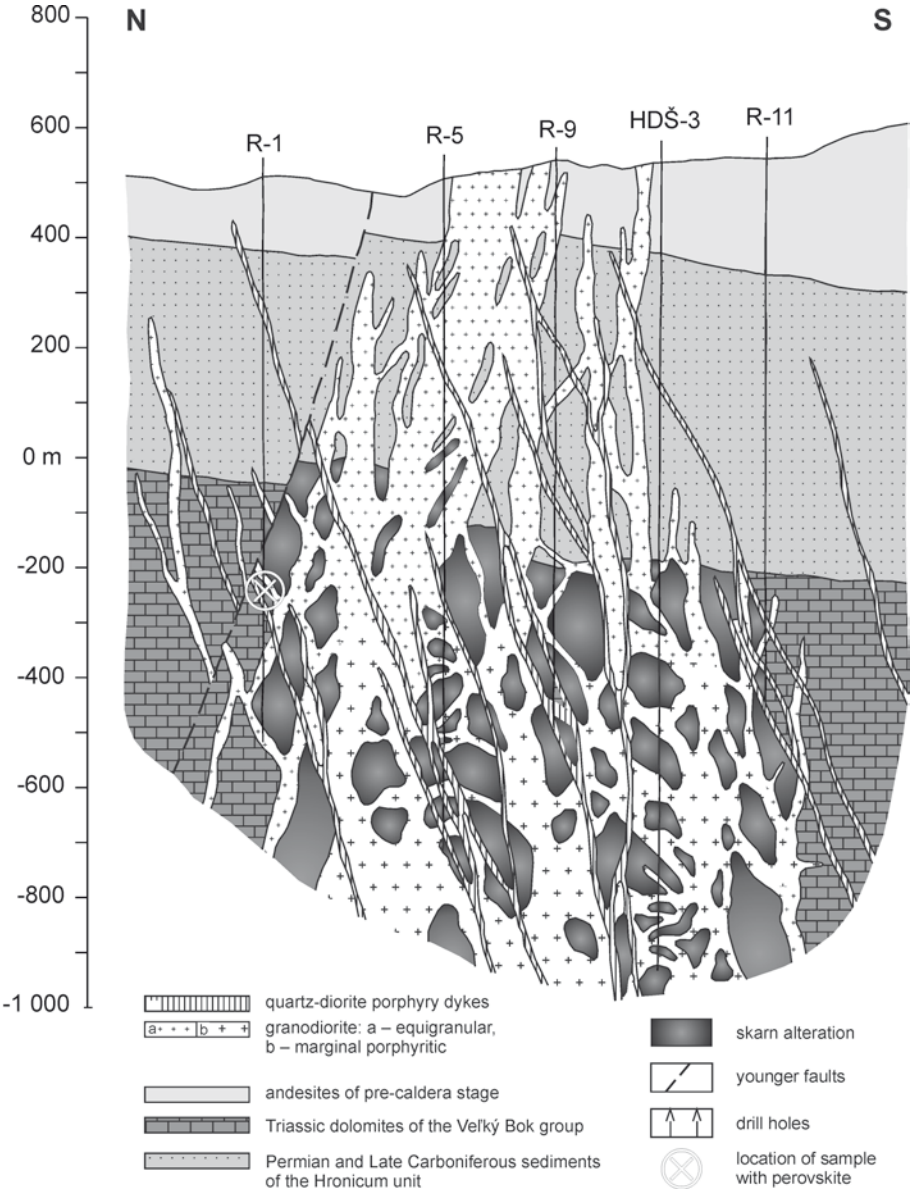

Fig. 1. Geological cross-section of the Vysoká – Zlatno skarn-porphyry deposit (modified after Marsina et al., 1993).

statistical errors from 0.03 to 0.15 wt.% (1 σ), depending on the element concentration. The electron-microprobe analytical data were reduced using the PAP routine. Perovskite compositions in oxide wt.% were calculated by empirical formulae on the basis of 3 oxygen atoms. The total iron content of perovskite formulae has been calculated as Fe^{3+}, due to strong preference of smaller ferric cation into the Ti^{4+} controlling *B*-site, in comparison to larger Fe^{2+} cation.

Selected trace elements of perovskite were investigated by LA-ICP-MS at the Department of Chemistry, Faculty of Science, Masaryk University, Brno, using a laser ablation system UP 213 (New Wave, USA) and an ICP-MS spectrometer Agilent 7500 CE (Agilent, Japan). A commercial Q-switched Nd: YAG laser ablation device works at wavelength of 213 nm. A sample was placed in the SuperCell (New Wave, USA). The ablated material was carried with helium (carrier gas), which transported the laser-induced aerosol to the inductively coupled plasma (1 l/min). A sample gas flow of argon was admixed to the helium carrier gas flow after the laser ablation cell. Therefore, the total gas flow was 1.6 l/min. Optimization of LA-ICP-MS conditions (gas flow rates, sampling depth, electrostatic lenses voltages of the MS) was performed with the glass reference material NIST SRM 610 in respect to maximum S/N ratio and minimum oxide formation (ThO^+/Th^+ counts ratio 0.2 %, U^+/Th^+ counts ratio 1.1 %). The LA-ICP-MS measurements used a single hole drilling mode for the duration of 60 seconds for each spot. Laser ablation was performed with laser spot diameter of 40 μm, laser fluency of 12 J cm^{-2} and repetition rate of 10 Hz. All element measurements were normalized on ^{43}Ca (281,000 ppm Ca = 39.32 wt.% CaO; this value approximates a real average composition of the studied perovskite).

Results

Perovskite forms disseminated, locally abundant, euhedral to subhedral crystals with pseudocubic or octahedral shape, usually 10 to 200 μm across, in monticellite and clintonite [Ca-mica, $CaMg_2Al(Al_3SiO_{10})(OH)_2$], rarely in andradite, spinel, magnetite, calcite, and anhydrite (Figs. 2a–d). Perovskite crystals occur as inclusions or in interstitial position with these minerals. Hydroxylellestadite,

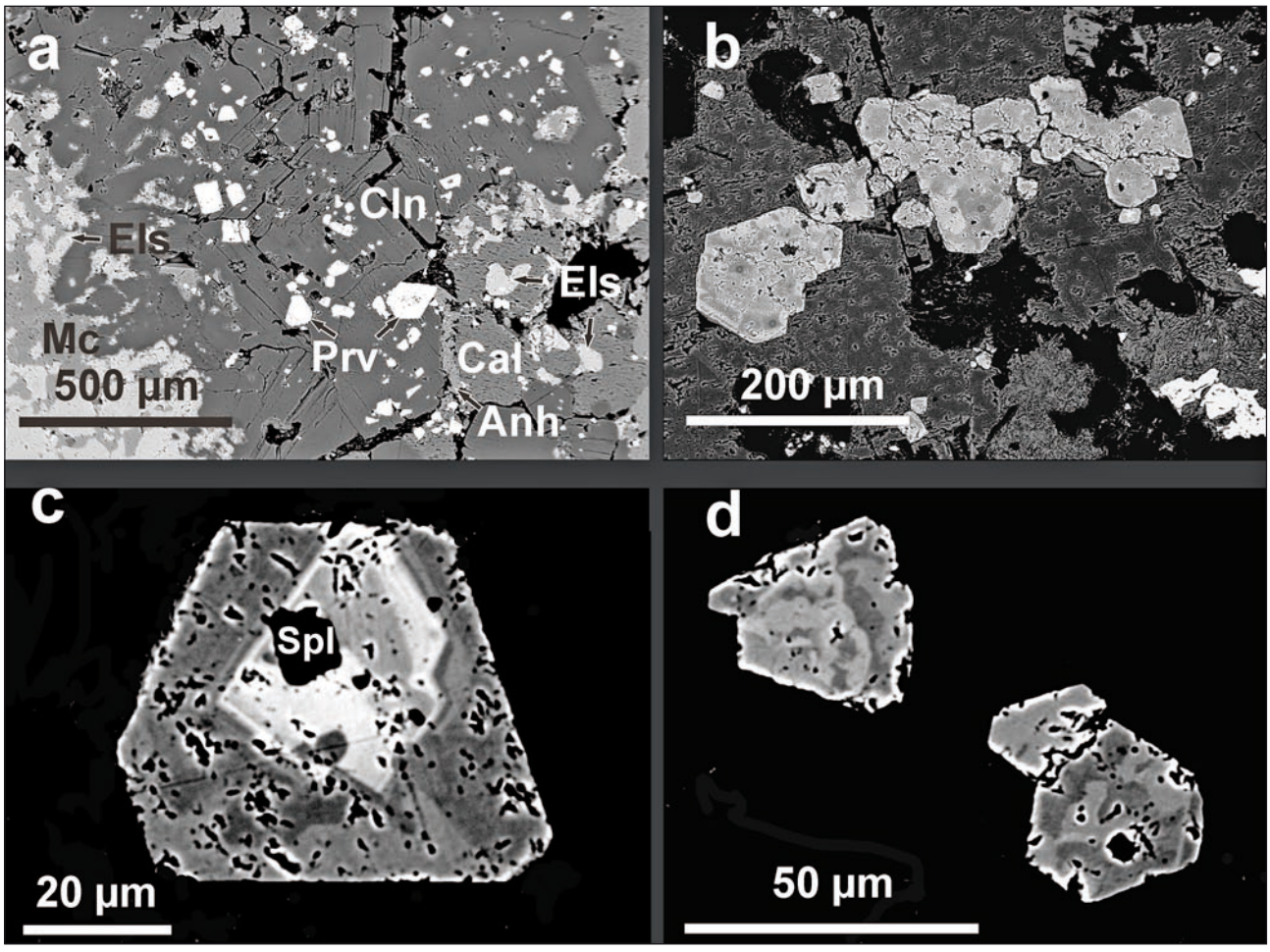

Fig. 2. BSE images of perovskite and associated skarn minerals from Vysoká – Zlatno. **a** – perovskite (Prv) in association with clintonite (Cln), monticellite (Mc), calcite (Cal), hydroxylellestadite (Els), and anhydrite (Anh); **b** – zonal perovskite crystals (light, medium and dark domains) in clintonite; **c** – euhedral perovskite crystal with inclusion of spinel (Spl) and regular zoning (very light to dark domains) in monticellite and clintonite; **d** – perovskite crystals with irregular light and dark domains in clintonite.

Tab. 1
Representative compositions of perovskite from the Vysoká – Zlatno skarn-porphyry deposit (wt.%)

Anal. No.	1B	7A	2B	5B	14A	13A	4B	17A	7B
Domain	dark	dark	medium	medium	light	light	very light	very light	very light
Composition						REE-rich	REE-rich	Th-rich	Th-rich
TiO_2	56.26	56.47	54.88	54.98	55.35	54.47	53.67	52.64	50.51
ZrO_2	0.16	0.26	0.65	0.67	0.06	0.05	0.52	0.24	0.31
ThO_2	0.08	0.15	0.15	0.13	0.40	0.06	0.68	2.14	5.48
UO_2	0.03	0.06	0.08	0.05	0.40	0.68	0.33	0.31	0.25
Al_2O_3	0.14	0.11	0.12	0.07	0.14	0.00	0.33	0.41	0.66
Fe_2O_3	1.23	1.44	1.84	1.82	1.67	1.33	1.93	2.58	2.78
La_2O_3	0.14	0.10	0.29	0.29	0.63	1.39	0.53	0.68	0.66
Ce_2O_3	0.39	0.48	0.83	0.92	1.97	3.69	1.38	1.71	1.85
Pr_2O_3					0.31	0.53		0.28	0.32
Nd_2O_3	0.14	0.19	0.32	0.41	0.70	1.18	0.51	0.62	0.68
Sm_2O_3					0.11	0.15			
CaO	40.47	40.49	39.57	39.53	39.00	36.33	38.65	38.09	36.46
Na_2O	0.07	0.00	0.00	0.00	0.05	0.23	0.05	0.00	0.13
Total	99.11	99.77	98.73	98.87	100.80	100.09	98.58	99.69	100.09
Formulae based on 3 oxygen atoms									
Ti	0.974	0.973	0.962	0.963	0.963	0.970	0.952	0.937	0.917
Zr	0.002	0.003	0.007	0.008	0.001	0.001	0.006	0.003	0.004
Al	0.004	0.003	0.003	0.002	0.004	0.000	0.009	0.011	0.019
Fe	0.021	0.025	0.032	0.032	0.029	0.024	0.034	0.046	0.050
Sum *B*	1.001	1.004	1.004	1.005	0.997	0.995	1.001	0.997	0.990
Th	0.000	0.001	0.001	0.001	0.002	0.000	0.004	0.012	0.030
U	0.000	0.000	0.000	0.000	0.002	0.004	0.002	0.002	0.001
La	0.001	0.001	0.002	0.002	0.005	0.012	0.005	0.006	0.006
Ce	0.003	0.004	0.007	0.008	0.017	0.032	0.012	0.015	0.016
Pr					0.003	0.005		0.002	0.003
Nd	0.001	0.002	0.003	0.003	0.006	0.010	0.004	0.005	0.006
Sm					0.001	0.001			
Ca	0.999	0.994	0.988	0.986	0.967	0.921	0.976	0.966	0.943
Na	0.003	0.000	0.000	0.000	0.002	0.010	0.002	0.000	0.006
Sum *A*	1.007	1.002	1.001	1.000	1.005	0.995	1.005	1.008	1.011
Sum cat.	2.009	2.006	2.006	2.005	2.002	1.990	2.006	2.005	2.001

locally sphalerite, chalcopyrite, pyrrhotite, valleriite [$4(Fe,Cu)S \cdot 3(Mg,Al)(OH)_2$], kimzeyite to kerimasite garnet, vesuvianite, clinochlore, brucite, and hydrotalcite (?) are associated minerals in the studied part of the skarn. Tiny inclusions of spinel (~10 μm in size) were observed in some perovskite crystals (Fig. 2c). Perovskite commonly shows regular to irregular zoning with darker and lighter domains under BSE (Figs. 2b–d). Locally, very light zonal euhedral domains (20 to 30 μm across), and medium to dark rim zones were observed (Fig. 2c). Conversely, some crystals display only irregular embayed dark and light domains (Fig. 2d). The different domains reflect compositional variations of perovskite; the lighter ones are enriched in REE´s (especially La to Nd), Th, and U, in comparison to the darker domains (Tab. 1). The regular domains in the central part of crystals (very light in BSE image) show ~3 to 6 wt.% $(La+Ce+Nd)_2O_3$ (0.03 to 0.05 *apfu*), light regular and irregular domains contain ~2 to 3 wt.% $(La+Ce+Nd)_2O_3$, whereas the medium and dark ones display only 0.7 to 1.6 wt.% $(La+Ce+Nd)_2O_3$, respectively. Cerium is dominant element among the REE´s (up to 3.6 wt.% Ce_2O_3, 0.032 *apfu* Ce). The LA-ICP-MS analyses show ca. 12 400 to 17 000 ppm of REE´s in bulk crystals, with distinct dominancy of light REE´s (LREE, La to Eu) over heavy REE´s (HREE, Gd to Lu+Y): the LREE/HREE ratio attains 13.5 to 18.6 (Tab. 2). The chondrite normalized REE diagram shows smooth patterns with regular decreasing of REE´s from La to Lu, only with little positive Ce and negative Eu anomalies (Fig. 3). The very light central domains also exhibit Th and U enrichment: up to 5.5 wt.% ThO_2 (0.03 *apfu* Th) and up to 0.7 wt.% UO_2 (0.004 *apfu* U), bulk Th and U contents achieve ~1 000 ppm Th and 730–970 ppm U (Tabs. 1 and 2).

Iron contents in perovskite attain 1.2 to 2.8 wt.% Fe_2O_3 (up to 0.050 *apfu* Fe), 11 500 to 15 800 ppm Fe in bulk crystals. Generally, Fe displays higher content in brighter (REE-rich) than darker (REE-poor) domains: 1.6 to 2.8 wt.% and 1.2 to 2.0 wt.%, respectively. Concentrations of Si and Al are generally low, usually 0.1 to 0.5 wt.%. Locally high LA-ICP-MS concentrations of Mg and Al are probably also due to tiny inclusions of spinel in perovskite (Tab. 2).

Studied perovskite shows also slightly enriched contents of Zr (~4 400 to 5 600 ppm), Hf (~200–260 ppm), Nb (~1 000–1 300 ppm), and Ta (~90–120 ppm), the

Tab. 2
LA-ICP-MS analyses of perovskite from the Vysoká – Zlatno skarn-porphyry deposit (ppm). LOD – limit of detection. Analyses 1 to 4 represent four spot measurements (40 μm diameter) in one larger crystal, analyses 5 to 7 are from three different smaller crystals.

Element	1	2	3	4	5	6	7	LOD
Li	<	<	<	<	<	<	<	573
Be	<	<	<	<	<	<	<	7
Na	<	<	<	<	<	180	<	122
Mg	111	167	429	96	852	1 549	7 162	8
Al	1 235	1 570	2 212	1 394	3 240	5 031	2 010	18
Si	295	413	557	334	1 400	1 145	564	180
P	<	<	<	<	<	<	<	29
K	<	<	<	<	<	<	<	352
Sc	<	<	<	<	<	<	<	21
V	36	29	36	44	34	34	34	1
Cr	<	31	59	62	32	189	90	19
Mn	27	29	30	21	34	40	99	10
Fe	11 572	12 465	13 480	12 754	12 814	12 718	15 838	6
Co	0.2	0.3	0.2	0.2	0.3	0.8	2.4	0.1
Ni	<	<	<	<	<	<	<	13
Zn	3	<	7	3	6	104	432	3
Ga	<	<	2	<	1.3	2	6	1.1
Sr	381	358	442	423	399	372	362	1
Y	339	342	370	344	344	327	317	0.1
Zr	5 018	4 805	5 651	4 554	4 425	5 591	5 032	0.5
Nb	1 149	1 151	1 264	1 168	1 102	1 040	1 225	0.1
Pd	4.8	4.9	4.8	<	4.4	<	<	4.4
Sn	106	104	105	86	85	124	106	8
Ba	<	<	<	<	1	<	<	1
La	2 725	2 744	2 890	2 799	2 585	2 449	2 535	0.3
Ce	6 992	9 428	8 911	7 437	8 330	6 390	5 443	0.0
Pr	623	605	740	819	693	622	636	0.1
Nd	3 127	2 816	2 901	2 763	2 722	2 505	2 422	0.1
Sm	395	499	504	474	404	457	450	0.1
Eu	101	84	96	97	90	82	81	0.1
Gd	298	283	350	298	234	312	281	0.1
Tb	33	39	35	32	32	31	31	0.1
Dy	153	144	150	137	123	145	157	0.3
Ho	21	19	23	19	19	19	19	0.1
Er	36	33	37	31	29	33	32	0.2
Tm	2.8	3.1	3.6	3.7	2.8	3.9	2.9	0.1
Yb	12	13	14	13	11	12	14	0.3
Lu	1.3	1.3	1.3	1.6	1.1	1.0	1.4	0.1
Hf	243	231	264	206	210	250	214	0.1
Ta	116	88	102	96	95	90	99	0.1
W	8	7	16	11	7	9	9	0.1
Pt	<	0.6	<	<	0.7	0.7	0.5	0.5
Pb	25	26	25	29	26	31	23	1.4
Th	1 052	1 007	1 034	1 014	980	1 067	1 112	0.1
U	786	765	971	737	740	731	762	0.1
Sum REE	14 858	17 054	17 027	15 271	15 622	13 389	12 422	
LREE/HREE	15.6	18.4	16.3	16.3	18.6	14.1	13.5	
wt. ratio								Average
Zr/Hf	20.7	20.8	21.4	22.2	21.1	22.3	23.6	21.7
Nb/Ta	9.9	13.0	12.4	12.2	11.6	11.6	12.4	11.9

weight Zr/Hf = 21.7, and Nb/Ta = 11.9 in average (Tab. 2). The concentrations of Sr and Na attain only up to 0.1 wt.% SrO and 0.2 wt.% Na_2O, respectively, in very light domains, but they are usually below detection limit of the electron microprobe (Tab. 1). The LA-ICP-MS concentrations of Sr achieve ~360 to 440 ppm, the contents of Na and other measured elements are usually below 200 ppm (Tab. 2).

The compositional variations reveal a near end-member perovskite composition: The molar proportion of $CaTiO_3$ varies from 94 % in very light to 98 % in the dark domains. Therefore, the compositional variations indicate only limited substitution of $REEFe^{3+}Ca_{-1}Ti_{-1}$, type. The Th(U)-rich domains caused deviation from the ideal substitution line (Fig. 4), possibly due to $Ca(Th,U^{4+})REE_{-1}$ exchange in *A*-site. Moreover, Zr (+Hf) probably replaces Ti ($ZrTi_{-1}$) in *B*-site of perovskite. Entry of Nb (+Ta) and REE´s into perovskite structure by $NaNbCa_{-1}Ti_{-1}$ and $NaREECa_{-2}$ couple substitutions are also possible in very restricted amounts but these mechanisms are questionable due to negligible Na contents.

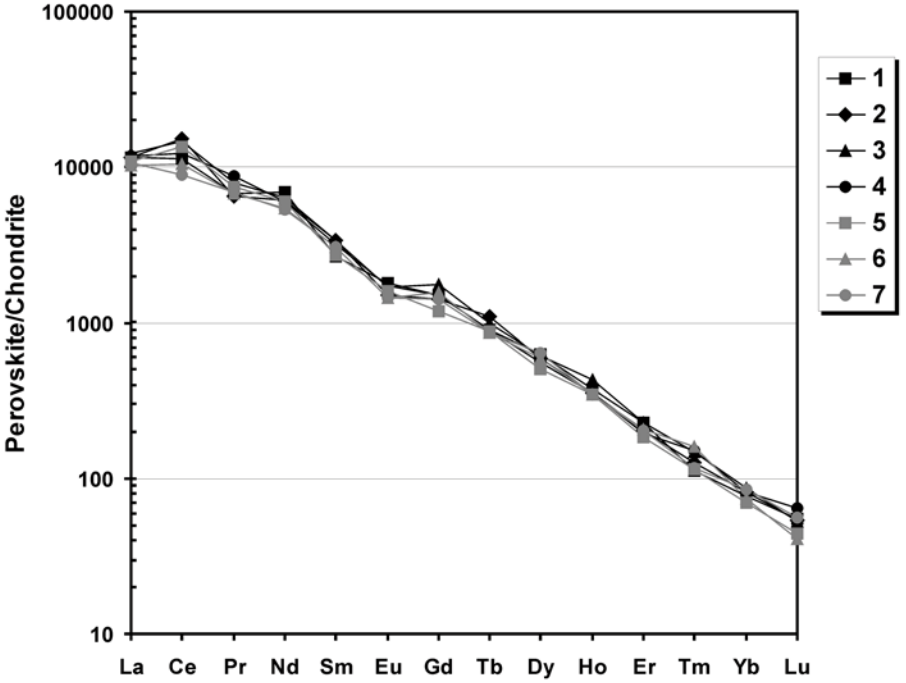

Fig. 3. The REE chondrite normalized plot of the Vysoká – Zlatno skarn--porphyry deposit. Numbers indicate LA-ICP-MS spot analyses, identical with numbers in Tab. 2. Carbonaceous chondrite (CI) concentrations used after McDonough and Sun (1995).

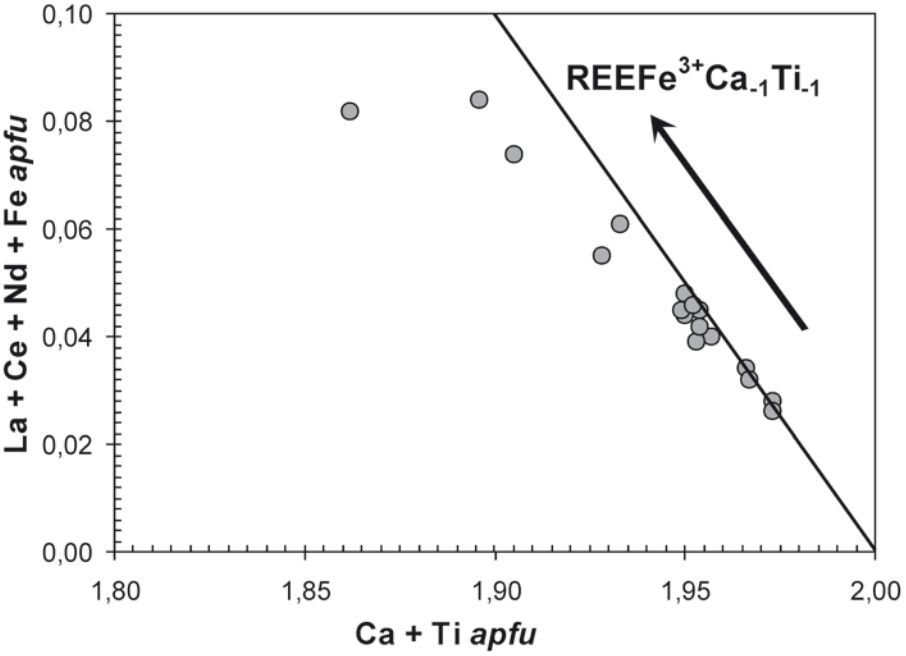

Fig. 4. The REE(Al,Fe^{3+})$Ca_{-1}Ti_{-1}$ substitution diagram of perovskite from the Vysoká – Zlatno skarn-porphyry deposit (atomic proportions). Note the deviation of REE-enriched compositions from ideal substitution line due to higher Th content (very light domains in perovskite).

The spinel inclusion in perovskite (Fig. 2c) shows $Mg_{0.92}Fe^{2+}_{0.08}Al_{1.85}Fe^{3+}_{0.13}Ti_{0.02}O_4$ composition. Moreover, perovskite locally associates with Mg-rich magnetite (5.5 wt.% MgO), with empirical formula $Fe^{2+}_{0.67}Mg_{0.30}Mn_{0.03}Fe^{3+}_{1.95}Al_{0.05}O_4$.

Concluding remarks

Perovskite represents a very rare mineral in the area of the Western Carpathians. Accessory perovskite forms tiny (~10 μm across) inclusions in biotite from Permian A-type granite at Pákozd, the Velence Mountains, Hungary (Pantó, 1975), the rocks belong to the Transdanubian Unit of the Inner Western Carpathians. Perovskite occurs in altered sill of olivine glimmerite, a member of Cretaceous alkali (ultra)basic hypoabyssal to volcanic suite (teschenite formation) from Międzyrzecze Górne near Bielsko-Biała, Poland in the Outer Western Carpathians (Włodyka and Karwowski, 2000). Recently, perovskite has been identified in meta-ultramafic rocks enclosed in serpentinite bodies of the Meliata Unit, in spherical fragments of meta-carbonatite (?) perovskite-clinopyroxene-grossular bearing rock on

Danková Hill near Dobšiná (Radvanec, 2009), and as euhedral crystals (up to 300 μm across) and intergrowths in pyroxene from serpentinized meta-peridotite in Dobšiná quarry (Putiš et al., 2011).

The presence of perovskite in the Vysoká – Zlatno Ca-Mg skarn represents its first reported occurrence from the contact metamorphic, skarn-related assemblages in the Western Carpathians, Slovakia. Besides magmatic occurrences, perovskite is also a widespread accessory mineral of high-temperature Ca-Mg skarns as a product of the high-temperature metasomatism of limestones in Ca-rich and Si-undersaturated environment (e.g., Joesten, 1976; Ivanova-Panayotova and Kanazirski, 1995; Anthony et al., 1997; Satish-Kumar et al., 2004; Rosa and Martin, 2010). In the Eastern Carpathians, a partly analogous occurrence of perovskite in association with spurrite, tilleyite, gehlenite, wollastonite, andradite, and hydroxylellestadite is described in the inner exoskarn zone from Cornet Hill, Metaliferi Mts., Romania (Marincea et al., 2001, 2010).

The REE distribution of the Vysoká – Zlatno perovskite shows strong dominancy of LREE over HREE, a characteristic feature of this mineral (e.g., Jones and Wyllie, 1984; Ulrych et al., 1988, 1996), corresponds to the similarity of ionic radii of $^{[12]}Ca^{2+}$ ($1.34 \cdot 10^{-10}$ m) and LREE, especially $^{[12]}La^{3+}$ ($1.36 \cdot 10^{-10}$ m) and $^{[12]}Ce^{3+}$ ($1.34 \cdot 10^{-10}$ m; Shannon, 1976). Sligtly positive Ce-anomaly of the studied perovskite is known in some occurrences from kimberlites and melilitites (Jones and Wyllie, 1984; Dawson et al., 1985), but it is absent in another perovskites from alkaline magmatic rocks (e.g., Ulrych et al., 1988, 1996). The entry of REE´s into the natural perovskite structure is usually yielded by the $NaREECa_{-2}$ substitution towards to loparite ($NaCeTi_2O_6$) end-member (e.g., Mitchell and Chakhmouradian, 1998), but the amount of Na is negligible in the Vysoká – Zlatno perovskite (Tabs. 1 and 2). Therefore, we propose the $REEFe^{3+}Ca_{-1}Ti_{-1}$ substitution mechanism (Fig. 3). Such substitution is not reported in natural perovskites but analogous orthorombic lanthanide-ferric compounds with perovskite structure ($LaFeO_3$, $CeFeO_3$, etc.) have been synthesized (Kumar and Verma, 2009).

Precipitation of perovskite in the Ca,Mg-skarn at Vysoká – Zlatno is probably connected with the peak, high--temperature (T > 600 °C) and prograde phase of contact metamorphic processes, represented by magnetite, spinel, andradite, and monticellite association, related to intrusion of Miocene granodiorite porphyry into Triassic dolomites. Regular primary zoning of perovskite indicates a decreasing activity of Fe, REE´s, Th and U during the contact metamorphic stage. However, irregular domains, rich or poor in these elements in some perovskite crystals, indicate a partial redistribution of these elements during the younger hydrothermal (?) overprint, possibly connected with fluid-driven, retrograde evolution stage of the Vysoká – Zlatno skarn-porphyry deposit.

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Perovskit z Ca-Mg skarnovo-porfýrového ložiska Vysoká – Zlatno, štiavnický stratovulkán

Perovskit ($CaTiO_3$) bol identifikovaný v Ca-Mg skarne na kontakte intrúzie miocénneho granodioritového porfýru a strednotriasových dolomitov skupiny Veľkého Boku na Cu-Au skarnovo-porfýrovom ložisku Vysoká – Zlatno v štiavnickom stratovulkáne, vo vrte R-1, v hĺbke 677 m. Skarnová mineralizácia je vyvinutá v alterovaných karbonátoch (exoskarny), ako aj na okrajoch intrúzie granodioritových porfýrov (endoskarny), v hĺbke cca 670 až 1 000 m (obr. 1). Minerály skarnu boli detailne opísané vo viacerých prácach (Zábranský, 1976; Kúšik, 1992; Marsina et al., 1995; Koděra et al., 2009). Perovskit vytvára idiomorfné až hypidiomorfné kryštály pseudokubického alebo oktaédrického habitu, obyčajne 10 až 200 μm veľké, resp. skupiny kryštálov v asociácii s monticellitom, clintonitom, hydroxylellestaditom, kalcitom, anhydritom (obr. 2), lokálne s andraditom, spinelom, magnetitom, sfaleritom, chalkopyritom, valleriitom, granátom zloženia kimzeyit až kerimasit, vesuvianitom, klinochlórom, brucitom a hydrotalkitom (?). Chemické zloženie perovskitu bolo študované pomocou elektrónovej mikroanalýzy (hlavné a vedľajšie prvky) a LA-ICP-MS (vedľajšie a stopové prvky). Kryštály perovskitu majú často pravidelnú alebo nepravidelnú zonalitu (obr. 2), spôsobenú variáciami obsahov REE, Th, U a Fe. Celkovo je perovskit z Vysokej – Zlatna relatívne blízky koncovému členu, obsahuje 94 – 98 mol. % $CaTiO_3$ (tab. 1). Niektoré domény majú zvýšené obsahy REE, najmä La, Ce a Nd; do 6 % $(La+Ce+Nd)_2O_3$ (do 0,05 *apfu* La + Ce + Nd), ako aj Th (max. 5,5 % ThO_2; 0,03 *apfu* Th) a U (max. 0,7 % UO_2; 0,004 *apfu* U). Obsahy Fe_2O_3 dosahujú 1,2 až 2,8 % (tab. 1). Analýzy LA-ICP-MS preukázali jasnú prevahu ľahkých REE (La-Eu; LREE) nad ťažkými REE (Gd-Lu + Y; HREE); priebehy chondritom normalizovaných kriviek REE poukazujú na ich pravidelný priebeh so slabou pozitívnou Ce anomáliou a nevýraznou negatívnou Eu anomáliou (obr. 3). Z ďalších vedľajších a stopových prvkov sú v perovskite z Vysokej – Zlatna mierne zvýšené obsahy Zr (~4 400 až 5 600 ppm), Hf (~200 až 260 ppm), Nb (~1 000 až 1 300 ppm) a Ta (~90 až 120 ppm), obsahy Na, Sr a ostatných stopových prvkov sú podľa LA-ICP-MS analýz veľmi nízke (tab. 2). Z možných substitúcií v študovanom perovskite je najpreukázateľnejšia $REEFe^{3+}Ca_{-1}Ti_{-1}$ (obr. 4). Jasná dominancia LREE nad HREE je typickou črtou perovskitu (Jones a Wyllie, 1984; Ulrych et al., 1988, 1996). Substitúcia $REEFe^{3+}Ca_{-1}Ti_{-1}$ nebola doteraz opísaná z prírodných perovskitov, avšak prítomnosť syntetických zlúčenín typu $LaFeO_3$, $CeFeO_3$ atď. s perovskitovou štruktúrou (Kumar a Verma, 2009) túto možnosť pripúšťa. Genéza perovskitu zo skarnovo-porfýrového ložiska Vysoká – Zlatno je na základe minerálnej asociácie spojená s prográdnym, vysokoteplotným metamorfno-metasomatickým procesom (nad 600 °C) v podmienkach obohatených Ca a ochudobnených Si. Analogické podmienky vzniku sa predpokladajú aj pre vznik perovskitu v podobných skarnových asociáciách, napr. v lokalite Cornet Hill v rumunských Karpatoch (Marincea et al., 2001, 2010). Prítomnosť nepravidelných domén v niektorých kryštáloch študovaného perovskitu však indikuje čiastočnú redistribúciu Fe, REE, Th a U, pravdepodobne spôsobenú mladším hydrotermálnym procesom v retrográdnej etape vzniku skarnovo-porfýrového ložiska Vysoká – Zlatno.