

Evolution of borate minerals from contact metamorphic to hydrothermal stages: Ludwigite-group minerals and szaibélyite from the Vysoká – Zlatno skarn, Slovakia

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Abstract Borate minerals of the ludwigite group (LGM) and szaibélyite in association with hydroxylclinohumite, clinocllore, a serpentine mineral, magnesian magnetite, spinel, magnesite, dolomite and sulphide minerals, occur in a magnesian exoskarn in the R-20 borehole located in the Vysoká – Zlatno Cu-Au porphyry-skarn deposit, located within the Štiavnica Neogene stratovolcano, Western Carpathians, central Slovakia. The skarn is developed along the contact of Miocene granodiorite to quartz-diorite porphyry and a Middle-Upper Triassic dolomite-shale-psammite-anhydrite sedimentary sequence. The boron minerals were investigated by electron probe micro-analyser (EPMA) and micro-Raman techniques. The source of boron could have been from the granodiorite/quartz diorite intrusion; however some supply of B from adjacent evaporite-bearing sediments is also possible. Based on textural and compositional data, the minerals originated during two stages. (1) An early high-temperature, contact-metamorphic and metasomatic stage comprises coarse-crystalline aggregate of LGM (types 1 to 3) in association with hydroxylclinohumite, magnetite, and rarely spinel inclusions in LGM. Compositional variations of LGM show a crystallization sequence from early azoprote $[\leq 17 \text{ wt\% TiO}_2; \sim 0.40 \text{ atoms pre formula unit (apfu) Ti}]$, which correspond to

$\leq 79 \text{ mol\%}$ of the $\text{Mg}_2(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_2(\text{BO}_3)$ end-member], Ti-Al-rich members of LGM, “aluminoludwigite” $[\leq 14 \text{ wt\% Al}_2\text{O}_3; \leq 0.53 \text{ apfu}, \leq 53 \text{ mol\% of Mg}_2\text{AlO}_2(\text{BO}_3) \text{ end-member}]$ and Al-rich ludwigite in the central zone of crystals, to Ti-Al-poor ludwigite in outer parts of crystals. (2) Minerals of the late retrograde serpentinization and hydrothermal stage form irregular veinlets and aggregates, including partial alteration of hydroxylclinohumite to the serpentine-group mineral and clinocllore, replacement of LGM by szaibélyite, formation of the latest generation of Fe-rich, Ti-Al poor ludwigite in veinlets (type 4), and precipitation of dolomite, magnesite and sulphide minerals (valleriite, sphalerite, chalcopyrite). The distinct compositional zoning of the LGM documents a complex evolution of the skarn beginning with a high-temperature stage 1 and ending with a low-temperature overprint, stage 2.

Keywords Ludwigite · Azoprote · Szaibélyite · Skarn · Contact metamorphism · Hydrothermal stage

Introduction

Borate minerals as natural compounds of $(\text{BO}_3)^{3-}$ and/or $(\text{BO}_4)^{5-}$ anionic groups with various cations are found in two principal modes of occurrence: (1) low-temperature sedimentary rocks, mainly evaporites, and (2) high-temperature metamorphic-metasomatic and magmatic assemblages, especially skarns, and rarely also in some granitic pegmatites (e.g., Anovitz and Grew 1996 and references therein). Formation of the borate minerals in the skarn systems are generally associated with the fluid-driven metamorphic and metasomatic processes in the contact aureoles between intrusive and extrusive magmatic rocks and adjacent carbonate-dominant lithologies, especially calcite and dolomite marbles (e.g., Pertsev 1991; Anovitz and Grew 1996; Grew et al. 1999; Woodford et al. 2001;

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Aleksandrov and Troneva 2011). Magnesian-iron borate minerals of the ludwigite group and szaibélyite [$\text{MgBO}_2(\text{OH})$] belong to the most characteristic boron phases of some magnesian skarns (e.g., Schaller and Vlisidis 1961; Kwak and Nicholson 1988; Marincea 1999a, b, 2000, 2001a, b; Aleksandrov and Troneva 2008, 2009, 2011; Tančić et al. 2012).

Ludwigite and associated minerals were identified, and briefly commented on, in an unpublished exploration report from a magnesian exoskarn in the R-20 borehole located in the Vysoká – Zlatno Cu-Au porphyry-skarn deposit in the Neogene Štiavnica stratovolcano, Western Carpathians, central Slovakia (Rojkovičová in Marsina et al. 1995). The skarn represents the first known occurrence of the borate minerals in the Western Carpathian area. The aims of this contribution are a description of the borate minerals and associated phases in detail, their crystal chemistry, micro-Raman spectroscopy, compositional variability and the evolutionary trend of ludwigite-group minerals, as tracers of the skarn formation beginning with a high-temperature, contact metamorphic and metasomatic stage and ending with a late, low-temperature hydrothermal overprint.

Regional geology

The Vysoká – Zlatno Cu-Au skarn – porphyry deposit is situated between Hodruša-Hámre and Uhliská villages near Banská Štiavnica town, Central Slovakia. The deposit occurs in the south-western part of the central zone of the Štiavnica stratovolcano, located in the Central Slovakia Neogene Volcanic Field in the inner side of the Carpathian arc of the Western Carpathians (Fig. 1a). The Cu-Au skarn-porphyry mineralization is related to a biotite-amphibole granodiorite stock and quartz-diorite porphyry dyke clusters with the zone of skarns at contacts between the granitic intrusive rocks and Middle to Upper Triassic carbonates, evaporites and pelitic to psammitic clastic sediments of the Veľký Bok Group (Koděra et al. 2010), Fig. 1b, c. The dyke clusters/stocks of granodiorite to quartz diorite porphyry belong to the Zlatno Intrusive Complex which was emplaced during the latest phase of the pre-caldera subvolcanic intrusion stage of the Štiavnica stratovolcano (13.5–12.9 Ma); the earlier intrusive phases of this stage have been dated at 13.3 and 13.4 ± 0.2 Ma by Rb-Sr isochrons based on whole-rocks and individual minerals (Chernyshev et al. 2013), in agreement with U-Th-Pb zircon dating by SHRIMP method (~ 13 Ma; Kohút and Danišík 2013).

The skarn mineralization is developed both in altered dolomites, limestones, anhydrite and gypsum evaporite beds and related clastic sediments (exoskarns) and on the margins of the porphyry intrusion (endoskarns) at a depth of over 700 m. The skarn rocks are variably represented by prograde and retrograde Mg- and Ca-skarn mineral assemblages (Koděra et al. 2010 and references therein). Prograde stage minerals of the

Mg-skarns include forsterite, diopside, spinel, magnetite, perovskite, and ilmenite. The retrograde mineral assemblage can be subdivided into an early-retrograde assemblage with phlogopite and chlorite, and late-retrograde minerals, including talc, serpentine, brucite, anhydrite, carbonates, hematite, sulphide minerals (pyrrhotite, pyrite, chalcopyrite, sphalerite, molybdenite, vallerite, tochilite), and gold.

In our study, borates and associated minerals have been studied in samples of Mg-skarn from the R-20 borehole material, from depth of 1174.1 m, located on the western margin of the deposit. The borehole is situated on the western slope of the Zlatno Valley, ca. 1.5 km NW of the Vysoká village and ca. 10 km SW of the Banská Štiavnica town. Geographical coordinates of the R-20 borehole are N $48^\circ 25.5'$ and E $18^\circ 46.2'$.

Analytical methods

Polished thin sections of the skarn rocks were studied under a research-grade optical microscope in cross-polarised transmitted light. Chemical compositions and internal zoning of minerals were investigated using the CAMECA SX 100 wavelength-dispersive electron probe micro-analyser (EPMA). Analytical conditions of 15 kV accelerating voltage, 10 to 20 nA sample current, a 3 to 5 μm beam diameter, and counting times of 20 s on peaks and 10 s on backgrounds were used. The following calibrant materials and spectral lines were used: barite (S $K\alpha$, Ba $L\alpha$), apatite (P $K\alpha$), wollastonite (Si $K\alpha$, Ca $K\alpha$), TiO_2 (Ti $K\alpha$), Al_2O_3 (Al $K\alpha$), metallic Cr (Cr $K\alpha$), fayalite (Fe $K\alpha$), rhodonite (Mn $K\alpha$), metallic Ni (Ni $K\alpha$), willemite (Zn $K\alpha$), forsterite (Mg $K\alpha$), SrTiO_3 (Sr $L\alpha$), albite (Na $K\alpha$), orthoclase (K $K\alpha$), LiF (F $K\alpha$), and NaCl (Cl $K\alpha$). The detection limits of the measured elements were 0.02 to 0.05 wt%, standard deviations (1σ) of the measured elements range from ± 0.02 to ± 0.6 wt%, depending on the element concentration. For data processing, the PAP procedure was used (Pouchou and Pichoir 1985).

Moreover, a part of the ludwigite group minerals were analyzed by a JEOL JXA 8530FE wavelength-dispersive EPMA, using an accelerating voltage of 20 kV, probe current 20 nA, beam diameter of 2 μm , and counting times 20 s on peak and 10 s on background. The calibrants, spectral lines, and detection limits were as follows: stibnite (Sb $L\alpha$, 54 ppm), rutile (Ti $K\alpha$, 24 ppm), ZrO_2 (Zr $L\alpha$, 54 ppm), cassiterite (Sn $L\beta$, 206 ppm), albite (Al $K\alpha$, 42 ppm), ScVO_4 (V $K\alpha$, 107 ppm), Cr_2O_3 (Cr $K\alpha$, 92 ppm), hematite (Fe $K\alpha$, 87 ppm), rhodonite (Mn $K\alpha$, 83 ppm), pentlandite (Ni $K\alpha$, 61 ppm), willemite (Zn $K\alpha$, 93 ppm), and diopside (Mg $K\alpha$, 39 ppm). The value of detection limit was calculated using following equation: $\sqrt{(2I/t)}$, where I is average intensity of the background X-rays and t is counting time of the background signals. The matrix effects were corrected by the conventional ZAF correction method.

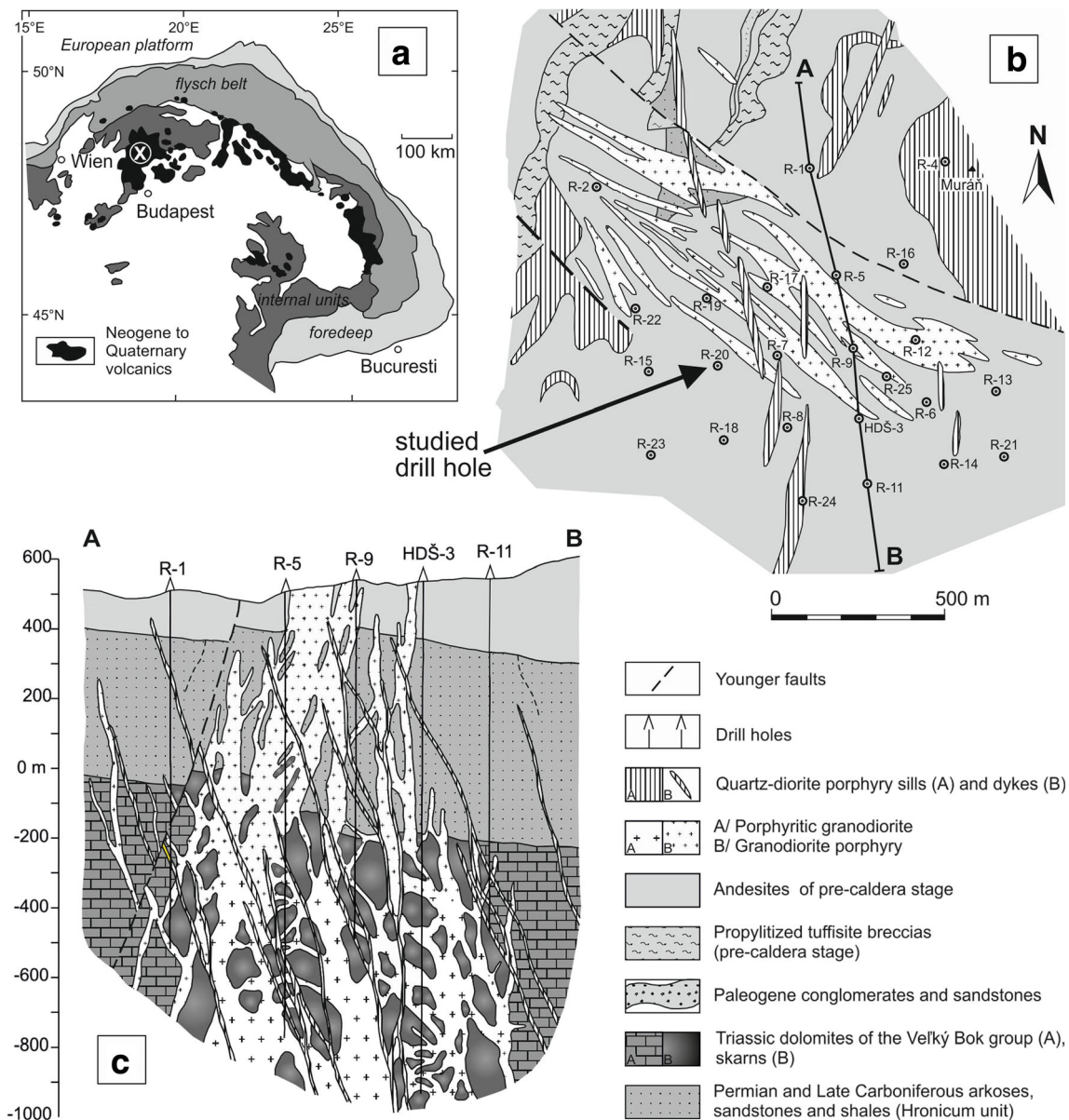


Fig. 1 Geological location (a), geological map (b) and cross-section (c) of the Vysoká – Zlatno Cu-Au porphyry-skarn deposit in the Štiavica Neogene stratovolcano, Western Carpathians (central Slovakia)

Content of B_2O_3 was calculated assuming ideal stoichiometry of the borate minerals (1 apfu for ludwigite-group minerals and szaibélyite). Content of H_2O was calculated by considering $(OH + F + Cl) = 1$ apfu for szaibélyite, $(OH + F + Cl) = 2$ apfu for hydroxylclinohumite, $(OH + F + Cl) = 8$ apfu for clinocllore, and $(OH + F + Cl) = 4$ apfu for serpentine-group mineral.

Raman spectroscopic measurements of thin sections were performed on Labram HR800 microspectrometer (Horiba Jobin-Yvon), based on the Olympus BX41 microscope with confocally coupled Czerny-Turner type monochromator (focal length 800 mm). A frequency-doubled Nd-YAG laser at 532 nm was used for excitation, 633 nm for verifying of luminescence effect. The Raman-scattered light was collected in 180° geometry through a $100\times$ objective lens with numerical

aperture 0.8 and dispersed by diffraction grating with 600 grooves per mm onto a cooled charge-coupled device (CCD) detector, with a total exposure time of 450 s. The system resolution was 2 cm^{-1} , band definition was improved using 5-fold sub-pixel shift. The grating turret accuracy was calibrated between the zero-order line (180° reflection) and the laser line at 0 cm^{-1} . Spectral accuracy was verified on the 734 cm^{-1} band of teflon. The number of Raman-active vibrational modes was calculated on the Bilbao crystallographic server (Kroumova et al. 2003) using the crystallographic data of Irwin and Peterson (1999) for ludwigite-group minerals and Takéuchi and Kudoh (1975) for szaibélyite. Bands were fitted and deconvoluted assuming Gaussian-Lorentzian band shapes.

Results

Borate minerals: ludwigite group and szaibélyite

Ludwigite-group minerals (LGM) commonly form massive black aggregates (>5 cm across) of numerous acicular, euhedral to subhedral prismatic crystals (usually 0.2 to 3 mm long). The LGM are associated with szaibélyite, hydroxylclinohumite, a serpentine-group mineral, magnetite, magnesite, dolomite (Fig. 2a, b), rarely clinocllore, spinel, valleriite (Fig. 2h), chalcopryrite, and sphalerite. The mineral textures and associations indicate two basic mineral stages: an older stage (1) with coarsely-crystalline aggregates of LGM with hydroxylclinohumite and

magnetite; and a younger stage (2) with a serpentine-group mineral, clinocllore, szaibélyite, late ludwigite veinlets, dolomite, magnesite and sulphide minerals.

In transmitted light in the polarizing microscope, LGM crystals are mostly opaque; however locally they are translucent with strong pleochroism in sections parallel to the c-axis with deep green ($X = Y$) to very dark green or reddish brown (Z) colour. In BSE images, LGM crystals show regular concentric, rarely oscillatory or irregular zoning caused by distinct compositional variations during their growth or partial alteration (Figs. 2c–f): the dark zones show enrichment in Mg, Al and Ti, in contrast to the pale zones which have larger amounts of Fe. The textural patterns and EPMA compositional data

Fig. 2 Back-scattered electron (BSE) images of borates and associated minerals in the Vysoká – Zlatno skarn (R-20 borehole, 1174.1 m depth). **a** aggregates of ludwigite-group minerals (LGM) and magnetite (Mag) of stage 1, with szaibélyite (Szb), stage 2; **b** hydroxylclinohumite (Hch) aggregate of stage 1, replaced by serpentine-group mineral along fracture-fillings (Srp) and magnesite (Mgs), stage 2; **c–f** internal zoning of LGM (stage 1) with central zones enriched in Ti, Mg and Al (types 1 and 2, *dark grey*) and outer zones enriched in Fe, poor in Ti and Al (type 3, mildly to *pale grey*); **g** zoned crystals of LGM, stage 1 (*grey*) replaced by narrow veinlets (stage 2) of the youngest ludwigite (type 4, *pale grey*) and magnesite (Mgs); **h** replacement of hydroxylclinohumite (Hch, stage 1) by late minerals of stage 2: platy aggregate of valleriite (Vlr), dolomite (Dol) and serpentine-group minerals (*dark grey* fracture fillings)

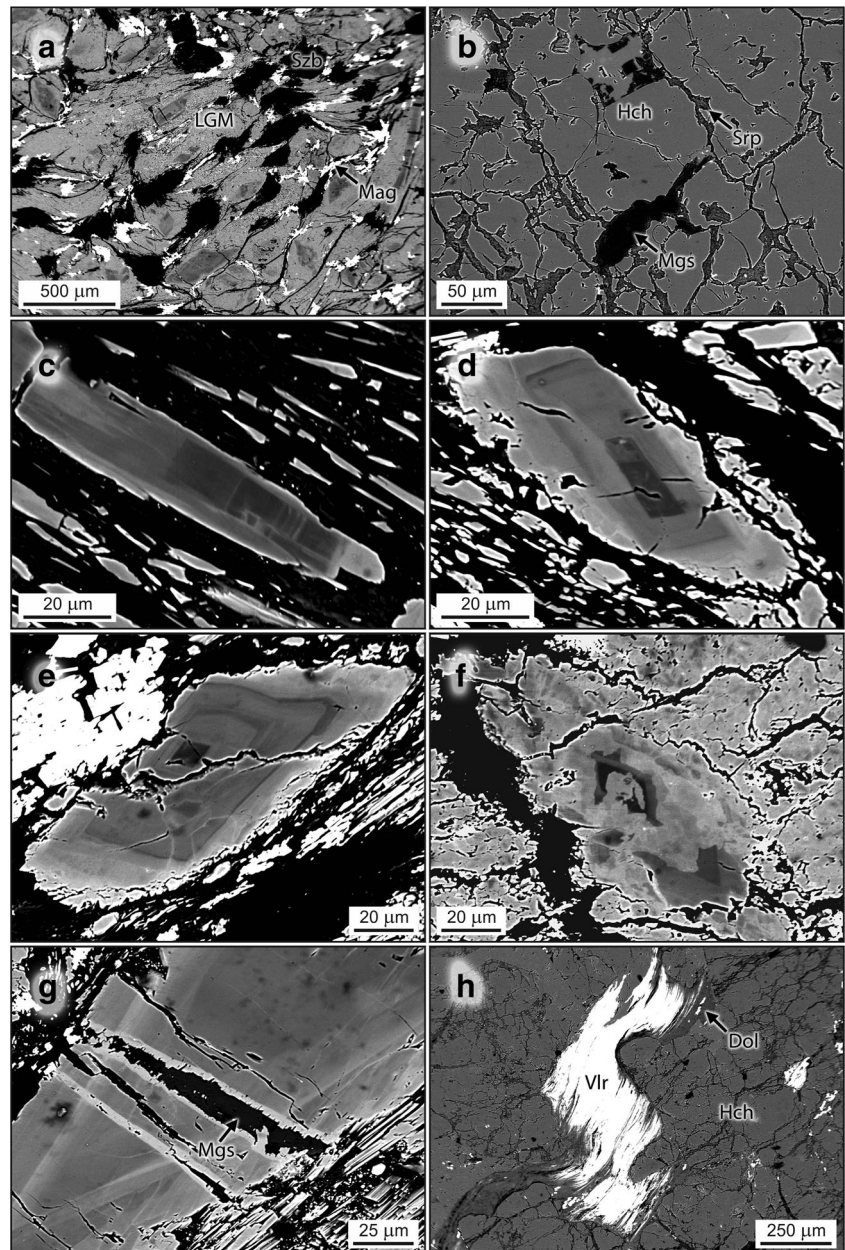


Table 1 Representative chemical compositions, calculated mineral formulae and mineral fractions of ludwigite-group minerals from the Vysoká – Zlatno skarn

Type	1	1	1	1	1	1
Position (zone)	Ti-Al-rich central	Ti-Al-rich central	Ti-Al-rich central	Ti-Al-rich central	Ti-Al-rich central	Ti-Al-rich central
Mineral	Azoproite	Azoproite	Azoproite	Azoproite	Al-Ldw	Al-Ldw
Analysis #	R-20E43	R-20A34	R-20E42	R-20A51	R-20A01	R-20A65
Oxide contents measured (in wt%)						
Sb ₂ O ₅	0.00	0.00	0.00	0.00	0.00	0.11
TiO ₂	15.44	14.32	12.36	11.02	4.96	2.92
ZrO ₂	0.64	0.61	0.42	1.01	0.06	0.37
SnO ₂	0.00	2.46	0.08	0.26	0.16	0.05
B ₂ O ₃ (calculated)	19.40	19.13	19.34	19.44	19.13	19.13
Al ₂ O ₃	4.42	2.67	6.99	7.89	11.90	13.10
V ₂ O ₃	0.29	0.40	0.30	0.22	0.12	0.25
Cr ₂ O ₃	0.00	0.00	0.02	0.04	0.04	0.00
Mn ₂ O ₃	0.05	0.02	0.00	0.03	0.09	0.05
Fe ₂ O ₃	5.53	7.24	7.74	8.29	14.81	16.52
FeO	2.82	1.24	3.19	1.61	3.93	2.76
NiO	0.00	0.03	0.00	0.00	0.02	0.00
ZnO	0.00	0.04	0.10	0.00	0.00	0.00
MgO	51.35	51.65	49.36	50.07	44.65	44.42
Total	99.95	99.81	99.91	99.89	99.88	99.68
Mineral formulae (in apfu)*						
B	1.000	1.000	1.000	1.000	1.000	1.000
Sb	0.000	0.000	0.000	0.000	0.000	0.001
Ti	0.347	0.326	0.278	0.247	0.113	0.066
Zr	0.009	0.009	0.006	0.015	0.001	0.005
Sn	0.000	0.030	0.001	0.003	0.002	0.001
Al	0.156	0.095	0.247	0.277	0.425	0.468
V	0.007	0.010	0.007	0.005	0.003	0.006
Cr	0.000	0.000	0.000	0.001	0.001	0.000
Mn	0.001	0.000	0.000	0.001	0.002	0.001
Fe ³⁺	0.124	0.165	0.174	0.186	0.338	0.377
Mg <i>M4</i>	0.355	0.365	0.286	0.265	0.117	0.075
Sum <i>M4</i>	0.999	1.000	0.999	1.000	1.002	1.000
Fe ²⁺	0.070	0.031	0.080	0.040	0.100	0.070
Mg <i>M1–3</i>	1.930	1.967	1.918	1.960	1.899	1.930
Ni	0.000	0.001	0.000	0.000	0.001	0.000
Zn	0.000	0.001	0.002	0.000	0.000	0.000
Sum <i>M1–3</i>	2.000	2.000	2.000	2.000	2.000	2.000
Fractions of end members (in mol%)**						
Ludwigite	12.0	16.2	16.7	18.3	32.2	36.6
Vonsenite	0.4	0.3	0.7	0.4	1.7	1.3
Al-Ldw	15.6	9.5	24.7	27.8	42.6	47.0
V-Ldw	0.7	1.0	0.7	0.5	0.3	0.6
Azoproite	69.5	65.2	55.7	49.5	22.6	13.3
Zr-Ldw	1.8	1.8	1.2	3.0	0.2	1.0
Sn-Ldw	0.0	6.0	0.2	0.6	0.4	0.2
Type	2	2	3	3	3	4
Position (zone)	Al-rich outer	Al-rich outer	Fe ³⁺ -rich outer	Fe ³⁺ -rich outer	Fe ³⁺ -rich outer	Fe ³⁺ -rich veinlets
Mineral	Al-Ldw	Ludwigite	Ludwigite	Ludwigite	Ludwigite	Ludwigite
Analysis #	R-20A66	R-20E36	R-20A26	R-20A31	R-20A32	R20E41
Oxide contents measured (in wt%)						
Sb ₂ O ₅	0.00	0.00	0.00	0.00	0.00	0.00
TiO ₂	0.85	0.33	0.07	0.04	0.02	0.00
ZrO ₂	0.00	0.03	0.00	0.00	0.00	0.00
SnO ₂	0.04	0.11	0.00	1.03	2.76	0.07
B ₂ O ₃ (calculated)	19.10	18.78	18.29	18.14	17.82	17.21
Al ₂ O ₃	14.19	11.62	6.10	4.68	2.52	0.40
V ₂ O ₃	0.00	0.00	0.00	0.04	0.00	0.00
Cr ₂ O ₃	0.00	0.04	0.00	0.06	0.00	0.00
Mn ₂ O ₃	0.11	0.05	0.03	0.04	0.03	0.00
Fe ₂ O ₃	19.75	23.98	32.21	32.94	33.93	38.78
FeO	2.63	2.64	0.75	0.63	1.69	8.08
NiO	0.00	0.00	0.00	0.02	0.00	0.00
ZnO	0.00	0.06	0.02	0.04	0.00	0.00

Table 1 (continued)

MgO	43.21	42.21	41.94	41.92	41.07	35.34
Total	99.88	99.86	99.42	99.61	99.83	99.88
Mineral formulae (in apfu)*						
B	1.000	1.000	1.000	1.000	1.000	1.000
Sb	0.000	0.000	0.000	0.000	0.000	0.000
Ti	0.019	0.008	0.002	0.001	0.001	0.000
Zr	0.000	0.000	0.000	0.000	0.000	0.000
Sn	0.001	0.001	0.000	0.013	0.036	0.001
Al	0.507	0.422	0.228	0.176	0.097	0.016
V	0.000	0.000	0.000	0.001	0.000	0.000
Cr	0.000	0.001	0.000	0.002	0.000	0.000
Mn	0.003	0.001	0.001	0.001	0.001	0.000
Fe ³⁺	0.451	0.557	0.768	0.792	0.830	0.982
Mg <i>M4</i>	0.020	0.009	0.001	0.015	0.036	0.001
Sum <i>M4</i>	1.001	0.999	1.000	1.001	1.001	1.000
Fe ²⁺	0.067	0.068	0.020	0.017	0.046	0.228
Mg <i>M1–3</i>	1.933	1.931	1.980	1.981	1.954	1.772
Ni	0.000	0.000	0.000	0.001	0.000	0.000
Zn	0.000	0.001	0.000	0.001	0.000	0.000
Sum <i>M1–3</i>	2.000	2.000	2.000	2.000	2.000	2.000
Fractions of end members (in mol%)**						
Ludwigite	43.7	54.0	76.0	78.8	81.0	87.0
Vonsenite	1.5	1.9	0.8	0.7	1.9	11.2
Al-Ldw	50.8	42.3	22.8	17.7	9.7	1.6
V-Ldw	0.0	0.0	0.0	0.1	0.0	0.0
Azoproite	3.8	1.6	0.4	0.2	0.2	0.0
Zr-Ldw	0.0	0.0	0.0	0.0	0.0	0.0
Sn-Ldw	0.2	0.2	0.0	2.6	7.2	0.2

S, Si, Ca, Sr, Ba, Na, K, F, and Cl contents were below detection limit

*Mineral formulae were calculated based on 5 oxygen atoms, 1 B atom and 3 (*M1–M4*) cations

**Abbreviations of end members: Al-Ldw = “aluminoludwigite” $\text{Mg}_2\text{AlO}_2(\text{BO}_3)$; V-Ldw = $\text{Mg}_2\text{VO}_2(\text{BO}_3)$; Zr-Ldw = $\text{Mg}_2(\text{M}_{0.5}\text{Zr}_{0.5})\text{O}_2(\text{BO}_3)$; Sn-Ldw = $\text{Mg}_2(\text{M}_{0.5}\text{Sn}_{0.5})\text{O}_2(\text{BO}_3)$

indicate four basic types (populations) of LGM in the investigated skarn (Table 1; Fig. 3): (1) Ti-rich compositions with

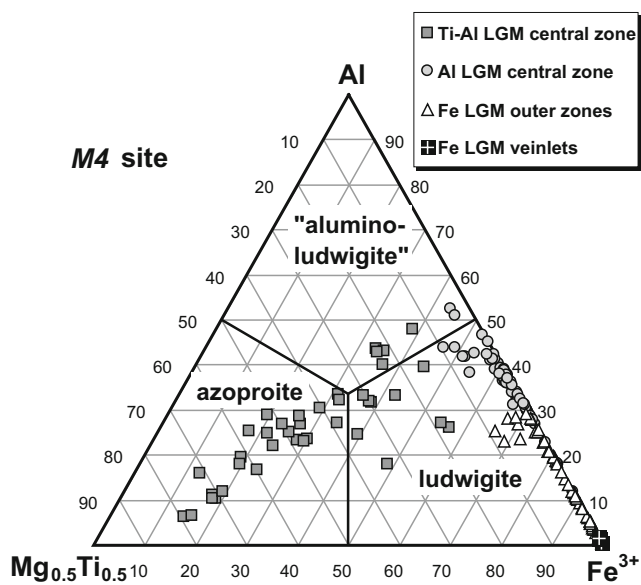


Fig. 3 Triangular Al– $\text{Mg}_{0.5}\text{Ti}_{0.5}$ – Fe^{3+} (*M4* site) classification diagram of LGM (atomic proportions) from the Vysoká – Zlatno skarn: Ti-Al-rich LGM central zone (type 1), Al-rich LGM central zone (type 2), Fe-rich LGM outer zones (type 3), and Fe-rich LGM veinlets (type 4)

moderate to high Al content, ranging from distinctly dominant azoproite [$\text{Mg}_2(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_2(\text{BO}_3)$] to intermediate Ti-Al-rich compositions, including Al-rich azoproite, Ti- Fe^{3+} -bearing “aluminoludwigite” [$\text{Mg}_2\text{AlO}_2(\text{BO}_3)$, an Al-dominant member of LGM] and Al-Ti-rich ludwigite [$\text{Mg}_2\text{Fe}^{3+}\text{O}_2(\text{BO}_3)$]; (2) Ti-poor and Al-rich LGM members, ranging from “aluminoludwigite” to Al-rich ludwigite; (3) the most common Fe^{3+} -rich and Ti-poor ludwigite compositions with negligible to low Al content; and (4) Fe^{2+} -enriched ludwigite, almost without Al and Ti. The Ti-Al- and Al-rich intermediate LGM (types 1 and 2) form small (~5 to 150 μm) euhedral to subhedral central zones of the crystals (Fig. 2c-f) which are overgrown by outer zones of Fe^{3+} -rich and Ti-(Al)-poor LGM of type 3. The latest ludwigite (type 4) forms narrow, ~1 to 30 μm thick veinlets, cutting the older LGM populations, in association with carbonate minerals (Fig. 2g). Compositional zoning in LGM crystals shows the an evolution from the oldest azoproite to the youngest ludwigite s.s. (from types 1 to 4) with an overall decrease in Mg, Ti and increase in Fe; the Al concentration increases from type 1 to 2 and subsequently decreases in the sequence types 3 to 4.

The Ti-Al-rich LGM members of type 1 (azoproite – “aluminoludwigite” – ludwigite solid solution) attains the highest Ti content: 3–17 wt% TiO_2 (0.07–0.40 apfu) which

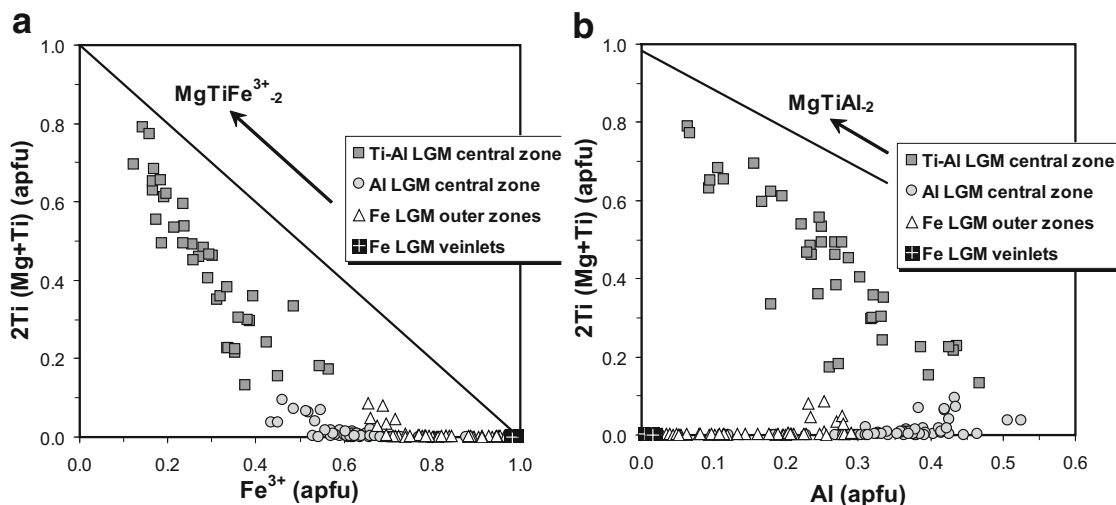


Fig. 4 Substitution MgTiFe^{3+}_2 (a) and MgTiAl_2 (b) diagrams (atomic proportions) of LGM compositional types from the Vysoká – Zlatno skarn: Ti-Al-rich LGM central zone (type 1), Al-

rich LGM central zone (type 2), Fe-rich LGM outer zones (type 3), and Fe-rich LGM veinlets (type 4)

corresponds to 13–79 mol% of the azoproite $[\text{Mg}_2(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_2(\text{BO}_3)]$ end-member. This population has the lowest concentrations of Fe_2O_3 (6–25 wt%; 0.14–0.57 Fe^{3+} apfu in the *M4* site), whereas the Al content is 2–13 wt% Al_2O_3 (0.10–0.49 apfu). The Ti-poor and Al-rich LGM compositions of type 2 (“aluminoludwigite” - ludwigite s.s.) show distinctly low Ti contents (0–2 wt% TiO_2 ; ≤ 0.05 apfu) but moderate to high Al concentrations (3–14 wt% Al_2O_3 ; 0.12–0.53 apfu) which correspond to 12–53 mol% of the $\text{Mg}_2\text{AlO}_2(\text{BO}_3)$ end-member (Table 1; Fig. 3). On the other hand, LGM of types 3 and 4 have a distinctly dominant ludwigite s.s. composition with the highest contents of Fe_2O_3 (28–40 wt%; 0.66–0.99 Fe^{3+} apfu in *M4* site) and negligible to very low Ti contents (≤ 1.8 wt% TiO_2 ; ≤ 0.04 apfu). Concentrations of Al_2O_3 range from 0.1 to 8 wt% (≤ 0.29 apfu) in type 3 but only 0.1 to 0.4 in type 4. The calculated content of the vonsenite $[\text{Fe}^{2+}_2\text{Fe}^{3+}\text{O}_2(\text{BO}_3)]$ molecule in LGM increases gradually from Ti-Al-rich compositions of type 1 (0.0 to 2.5 mol%), through Al-rich type 2 (0.1 to 5.4 mol%), to ludwigite of type 3 (0.0 to 13 mol%) and type 4 (8.5 to 11 mol%). In contrast, MgO content of LGM gradually decreases from 42 to 52 wt% (1.98–2.35 apfu) in type 1 to 35–37 wt% (1.77–1.83 apfu) in type 4.

The contents of other constituents in LGM are usually low or under the detection limit of the EPMA. However, Sn, Zr and V rarely attain elevated concentrations (Table 1): 2.5 to 3.2 wt% SnO_2 (0.03–0.04 apfu), 0.4 to 1.0 wt% ZrO_2 (0.01–0.02 apfu), and 0.2 to 0.5 wt% V_2O_5 (≤ 0.01 apfu) in Ti-Al-rich LGM compositions of type 1; Sn-enriched analyses were locally documented also in ludwigite of type 3 (1.0–2.8 wt% SnO_2 ; 0.01–0.04 apfu). The compositional variations indicate the following main substitution mechanisms in the studied LGM (Table 1, Figs. 3 and 4): $\text{Fe}^{2+} = \text{Mg}^{2+}$ in *M1–3* sites for all compositions, $\text{Mg}^{2+} +$

Ti^{4+} (Sn^{4+} , Zr^{4+}) = $2(\text{Fe}^{3+}$, Al) or $\text{Mg}^{2+} + \text{Ti}^{4+} = 2\text{Fe}^{3+}$ and $\text{Mg}^{2+} + \text{Ti}^{4+} = 2\text{Al}^{3+}$ in *M4* site mainly for analyses including high Ti contents (type 1), and Al^{3+} (V^{3+}) = Fe^{3+} in *M4* site for compositions with a small amount of Ti but moderate to high Al contents (types 2 and 3).

Szaibélyite $[\text{MgBO}_2(\text{OH})]$ forms irregular, usually 0.1 to 0.4 mm large aggregates of acicular crystals replacing LGM, in association with magnetite (Fig. 2a). The EPMA analyses of szaibélyite show a relatively homogenous composition without significant impurities (Table 2). Concentrations of iron attain 0.5 to 1.2 wt% FeO (up to 0.014 apfu), Cr and Mn contents are below 0.3 wt% of oxide (≤ 0.003 apfu), the $\text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ atomic ratio achieves around 0.99.

Associated minerals

Hydroxylclinohumite $[\text{Mg}_9(\text{SiO}_4)_4(\text{OH})]$ is a common mineral on the investigated skarn, forming granular aggregates of subhedral, rarely euhedral crystals (usually 0.1 to 0.6 mm across), in association with LGM, a younger serpentine mineral and magnesite (Fig. 2b), clinochlore and dolomite. Hydroxylclinohumite has a relatively uniform composition with a negligible content of Fe (up to 0.5 wt% FeO) and Mn (≤ 0.14 wt% MnO) and distinct dominance of the hydroxyl anion over fluorine: $\text{OH}/(\text{OH} + \text{F})$ ratio ranges from 0.71 to 0.85, fluorine concentration are 0.9 to 1.8 wt%, 0.30–0.58 F apfu (Table 3).

Clinochlore occurs as platy crystals or irregular aggregates, up to 1 mm in size, it is usually associated with late dolomite and replaces hydroxylclinohumite. Clinochlore is highly magnesian [atomic $\text{Mg}/(\text{Mg} + \text{Fe}^{2+}) = 0.97$ to 0.99] and contains ~1.1 to 1.8 Al apfu (Table 4). Variations in Al, Fe and Mg indicate the presence of a $^{\text{O}}(\text{Al},\text{Fe})^{3+} + ^{\text{T}}\text{Al} = ^{\text{O}}(\text{Mg},\text{Fe})^{2+} + ^{\text{T}}\text{Si}$ coupled substitution in clinochlore (Fig. 5).

Table 2 Representative chemical compositions and calculated mineral formulae of szaibélyite from the Vysoká – Zlatno skarn

Analysis #	R-20B01	R-20E25	R-20E32	R-20D47
Oxide contents measured (in wt%)				
SO ₃	0.00	0.00	0.09	0.23
B ₂ O ₃ (calculated)	41.08	41.05	41.07	40.90
Al ₂ O ₃	0.00	0.11	0.15	0.11
Cr ₂ O ₃	0.00	0.28	0.13	0.00
Fe ₂ O ₃	0.00	0.00	0.00	0.00
FeO	0.53	0.69	0.47	1.17
MnO	0.22	0.12	0.11	0.14
MgO	47.07	46.85	47.00	46.42
CaO	0.11	0.00	0.00	0.00
H ₂ O (calculated)	10.63	10.62	10.63	10.58
Total	99.64	99.73	99.64	99.54
Mineral formulae (in apfu)*				
B	1.000	1.000	1.000	1.000
S	0.000	0.000	0.001	0.002
Al	0.000	0.002	0.002	0.002
Cr	0.000	0.003	0.001	0.000
Fe ³⁺	0.000	0.000	0.000	0.000
Fe ²⁺	0.006	0.008	0.006	0.014
Mn	0.003	0.001	0.001	0.002
Mg	0.990	0.983	0.986	0.975
Ca	0.002	0.000	0.000	0.000
Sum of cations	1.001	0.997	0.996	0.993
O	2.000	2.000	2.000	2.000
OH	1.000	1.000	1.000	1.000
Sum of anions	3.000	3.000	3.000	3.000
Mg/(Mg + Fe ²⁺)	0.99	0.99	0.99	0.99

Si, Ti, Ni, Sr, Ba, Na, K, F, and Cl contents were below detection limit

*Mineral formulae were calculated based on 3 anions, 1 B atom, 1 (OH) anion and valence calculation

A serpentine-group mineral forms aggregates filling irregular veinlets and cracks (up to 50 µm across) in hydroxylclinohumite (Figs. 2b, h). The Mg-dominant serpentine phase shows small admixtures of Al, Cr and Fe (up to 0.1 apfu; Table 5).

Magnesian magnetite is a relatively common mineral of the skarn assemblage, it occurs as euhedral to anhedral crystals in association with LGM, hydroxylclinohumite and szaibélyite (Fig. 2a). Magnetite has elevated contents of Mg (2.2 to 5.0 wt% MgO; 13 to 27 mol% magnesioferrite) and low Mn (0.1 to 0.6 wt% MnO; 0.4 to 1.8 mol% jacobsonite), concentrations of Al are negligible, ≤0.1 wt% Al₂O₃ (Table 6). Spinel forms very rare tiny anhedral inclusions in LGM, their compositions corresponding to spinel (95–96 mol% MgAl₂O₄) with 4.3 to 5.3 wt% Fe₂O₃ (3.9 to 4.9 mol% magnesioferrite) and low concentrations of Cr and Ti (Table 6).

Carbonate minerals are represented by dolomite and magnesite (both confirmed by EPMA analyses); they form late fracture fillings in LGM together with the youngest ludwigite veinlets of type 4 (Fig. 2g) or they form irregular aggregates which replace older hydroxylclinohumite and probably also clinocllore. Locally, curved fibrous aggregates of valleriite [4(Fe,Cu)S·3(Mg,Al)(OH)₂] in association with hydroxylclinohumite, dolomite and serpentine-group mineral (Fig. 2h), and tiny isolated grains of chalcopryrite and sphalerite (up to 20 µm in size) were found in hydroxylclinohumite and dolomite.

Raman spectroscopy of borate minerals: description and interpretation

We investigated LGM of various compositions (types 1 to 4) in the Vysoká – Zlatno skarn by the micro-Raman spectroscopy. All the spectra show striking similarities at the low- and high-energy ends, but some distinct differences in the middle part of the spectra (Fig. 6). The vibrations between 60 and 120 cm⁻¹ are the most intense in Ti-Al-poor ludwigite of types 3 and 4 (Fig. 6 - spectrum 1; Table 1, anal. R-20E41), in contrast to the rest of the spectra where they are strongly suppressed in intensity compared to the other measured phases. The bands around 73–74, 83, 92–93, 107–108 and 116–118 cm⁻¹ are common for all the minerals, while the weak band at 100 cm⁻¹ of Al-rich ludwigite of type 2 (Fig. 6 - spectrum 2; Table 1, anal. R-20E36), and azoprote of type 1 (Fig. 6 - spectra 3 and 4; Table 1, anal. R-20E42 and R-20E43, respectively) is only pronounced only as a shoulder in ludwigite (spectrum 1). In the middle region (120–800 cm⁻¹) there is increasing efficiency in Raman scattering, band diversity and certain band shifts in the order ludwigite – Al-rich ludwigite – azoprote. In the higher energy region, the spectrum of Al-rich ludwigite has a small but distinct band at 959 cm⁻¹, split into a doublet at 943 and 955 cm⁻¹ in azoprote. In all minerals we observe a broad feature with unresolved bands between 1150 and 1400 cm⁻¹ rising in intensity from ludwigite through Al-rich ludwigite to azoprote, the latter two having distinct maxima at 1193 and 1187 cm⁻¹, respectively.

The interpretation of LGM Raman spectra is not a routine due to a lack of reference spectra. The available data are records of synthetic Fe₃O₂(BO₃) and Ni₂FeO₂(BO₃) (Leite et al. 2002) and natural members of the ludwigite - vonsenite series [Frost et al. 2014; RRUFF database (cf. Lafuente et al. 2015); Enholm 2016]. Raman spectra of selected oxyborate minerals including azoprote published in Frost (2011) are doubtful as all their Raman bands unequivocally point to calcite (e.g., see the RRUFF database). Presented spectra of ludwigite (Fig. 6 - spectrum 1) are generally closely comparable to the published data. Raman bands up to 280 cm⁻¹ occurring in all our spectra (Fig. 6) are assigned to external vibrations of [BO₃] and [FeO₆] groups (Leite et al. 2002; Enholm 2016). The activity

Table 3 Representative chemical compositions and calculated mineral formulae of hydroxylclinohumite from the Vysoká – Zlatno skarn

Analysis #	R-20A02	R-20A03	R-20D01	R-20D03	R-20D04
Oxide contents measured (in wt%)					
SiO ₂	38.48	37.84	38.08	38.19	37.92
Al ₂ O ₃	0.00	0.00	0.04	0.20	0.51
Fe ₂ O ₃	0.00	0.31	0.38	0.00	0.00
FeO	0.46	0.00	0.06	0.23	0.34
MnO	0.11	0.14	0.05	0.11	0.11
MgO	57.49	57.42	57.14	56.75	56.83
CaO	0.04	0.14	0.00	0.03	0.00
Na ₂ O	0.00	0.00	0.12	0.12	0.00
H ₂ O (calculated)	2.12	2.20	2.03	2.17	2.43
F	1.59	1.39	1.75	1.44	0.89
O = F	−0.67	−0.59	−0.74	−0.61	−0.37
Total	99.62	98.85	98.91	98.63	98.66
Mineral formulae (in apfu)*					
Si	4.009	3.973	3.995	4.013	3.983
Al	0.000	0.000	0.005	0.025	0.063
Fe ³⁺	0.000	0.025	0.030	0.000	0.000
Fe ²⁺	0.040	0.000	0.006	0.020	0.030
Mn	0.010	0.012	0.004	0.010	0.010
Mg	8.928	8.988	8.936	8.891	8.899
Ca	0.004	0.016	0.000	0.003	0.000
Na	0.000	0.000	0.024	0.024	0.000
Sum <i>T + M</i>	12.991	13.014	13.000	12.986	12.985
OH	1.476	1.539	1.419	1.521	1.704
F	0.524	0.462	0.581	0.479	0.296
Sum <i>X</i>	2.000	2.001	2.000	2.000	2.000
O	16.000	16.000	16.000	16.000	16.000
OH/(OH + F)	0.74	0.77	0.71	0.76	0.85

S, Ti, Cr, Ni, Sr, Ba, K, and Cl contents were below detection limit

*Mineral formulae were calculated based on 18 cations, 2 (OH) + F anions and valence calculation

between 300 and 500 cm^{−1} may be attributed to *M*-O stretching and bending modes (Leite et al. 2002; Enholm 2016). A band at 668 cm^{−1} is assigned to the ν_4 bending mode of [BO₃] group (Leite et al. 2002; Frost et al. 2014; Enholm 2016). In some oxyborates splitting of this mode has been reported and explained as due to lower site symmetry than that of (BO₃)^{3−} ion (Enholm 2016). This splitting is pronounced in our azoproite (Fig. 6 - spectra 3 and 4), where it probably affects all the spectral region between 500 and 800 cm^{−1}. This phenomenon could be explained by the Mg²⁺ + Ti⁴⁺ (Sn⁴⁺, Zr⁴⁺) = 2(Fe³⁺, Al) substitution causing distortion of site symmetries and subsequent loss of degeneracy in internal modes of the [BO₃] group in LGM. In accordance with Enholm (2016), this splitting does not occur in our ludwigite (Fig. 6 - spectrum 1). Broad band between 1150 and 1400 cm^{−1} (Fig. 6) can be assigned to ν_3 stretching mode (Enholm 2016). Band shifts in the Raman spectra are distinctive between ludwigite, Al-rich ludwigite and azoproite, but

complex cation substitutions between dominant cations (Ti, Al, Fe and Mg) hampered a reliable interpretation. Between the spectra 3 and 4 (Fig. 6) which represent azoproite compositions with 0.28 and 0.35 Ti apfu, respectively (Table 1, anal. R-20E42 and R-20E43) the shifts are minor but their equivalence is obvious. Here we can correlate the Ti-substitution with downshifts of the bands at 354, 379 and 716 cm^{−1} towards 349, 375 and 713 cm^{−1}, respectively.

The Raman spectra of szaibélyite from the Vysoká – Zlatno skarn (Fig. 7) are comparable to published data (Galuskina et al. 2008; Frost et al. 2015; Lafuente et al. 2015). Two narrow peaks at 836 and 3559 cm^{−1} are dominant in the spectra of the studied szaibélyite (Fig. 7). Weak bands in the region from 80 to 350 cm^{−1} (the most intensive are at 296, 327, 345 cm^{−1}) can be assigned to lattice vibrations or external vibrations of functional groups and internal vibrations of [MgO₆] octahedra. In other similar borates, the internal symmetric stretching vibration band ν_1 of the [BO₃] group usually appears in the region

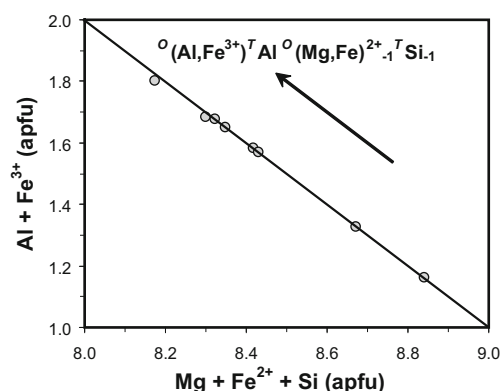
Table 4 Representative chemical compositions and calculated mineral formulae of clinocllore from the Vysoká – Zlatno skarn

Analysis #	R-20B05	R-20D15	R-20D17	R-20D18
Oxide contents measured (in wt%)				
SiO ₂	34.09	33.70	33.46	36.46
Al ₂ O ₃	12.38	14.90	16.39	9.79
Fe ₂ O ₃	2.69	0.42	0.00	1.10
FeO	0.91	2.20	1.77	2.12
MgO	36.58	35.67	35.32	37.57
H ₂ O (calculated)	12.68	12.77	12.82	12.76
Cl	0.15	0.04	0.03	0.08
O = Cl	−0.03	−0.01	−0.01	−0.02
Total	99.45	99.68	99.78	99.86
Mineral formulae (in apfu)*				
Si	3.216	3.162	3.122	3.420
Al <i>T</i>	0.784	0.838	0.878	0.580
Sum <i>T</i>	4.000	4.000	4.000	4.000
Al <i>O</i>	0.593	0.810	0.924	0.502
Fe ³⁺	0.191	0.029	0.000	0.078
Fe ²⁺	0.072	0.173	0.138	0.167
Mg	5.144	4.989	4.914	5.253
Sum <i>O</i>	6.000	6.001	5.976	6.000
OH	7.976	7.994	7.995	7.987
Cl	0.024	0.006	0.005	0.013
Sum <i>X</i>	8.000	8.000	8.000	8.000
O	10.000	10.000	10.000	10.000
Sum of cations	10.000	10.001	9.976	10.000
Sum of anions	18.000	18.000	18.000	18.000
Al total	1.377	1.648	1.802	1.082
Mg/(Mg + Fe ²⁺)	0.99	0.97	0.97	0.97

Ti, Cr, Mn, Ca, Sr, Ba, K, and F contents were below detection limit

*Mineral formulae were calculated based on 18 oxygen atoms, 8 (OH) + Cl anions, 10 cations and valence calculation

of 880–1017 cm^{−1}, out-of-plane bending ν_2 in region 705–790 cm^{−1}, asymmetric stretching vibration bands ν_3 in region

**Fig. 5** Substitution $O(\text{Al,Fe}^{3+})T\text{Al } O(\text{Mg,Fe})^{2+}_1\text{Si}_1$ diagram (atomic proportions) of clinocllore from the Vysoká–Zlatno skarn

1200–1370 cm^{−1} and in-plane bending ν_4 in region 510–650 cm^{−1} (Li et al. 1994; Wopenka et al. 1999; Galuskina et al. 2008). In the studied szaibélyite, spectral bands of [BO₃] appear shifted to lower energies (Fig. 7), where the narrow strong band at 836 cm^{−1} may correspond to symmetric stretching modes ν_1 of the [BO₃] group. The twin broad band around 1270 and at 1284 cm^{−1} may be attributed to asymmetric stretching modes ν_3 of [BO₃], where splitting is probably an effect of either an isotope substitution of ¹¹B and ¹⁰B (Li et al. 1994), or substitution of hydroxyl groups for oxygen. According to Frost et al. (2015), [BOH] in-plane bending modes in szaibélyite occur in the region 1140–1320 cm^{−1}. Two narrow bands at 3559 and 3567 cm^{−1} are expression of stretching O–H vibrations in the [BO₂(OH)] groups. Two bands in this region probably reflect two positions of [OH] groups in szaibélyite structure (Grice 2008). Other weak broad bands at 3520 cm^{−1} and in the region 3635–3670 cm^{−1} may be assigned to O–H vibrations in hydroxyl groups. Unfortunately, small size of the studied crystals did not allow oriented polarized measurements that are necessary to confirm the assignment of the Raman vibrations.

Discussion

Crystal chemistry of ludwigite-group minerals

The structure of LGM consists of zig-zag walls of edge-sharing octahedra, linked by sharing corners and by BO₃ planar triangles where four octahedral sites (*M1* to *M4*) can be recognized (Bonazzi and Menchetti 1989; Takéuchi and Kogure 1992; Appel and Brigatti 1999; Tančić et al. 2012). The *M1* to *M4* octahedral sites contain divalent to trivalent, rarely also tetravalent and pentavalent, cations (Mg²⁺, Fe²⁺, Ni²⁺, Mn²⁺, Al³⁺, Fe³⁺, Mn³⁺, V³⁺, Cr³⁺, Sb³⁺, Ti⁴⁺, Sn⁴⁺, and Sb⁵⁺) with some degree of disorder. For example, Mg²⁺ is distributed over all *M1*–*M4* sites, Fe²⁺ occupies *M1* to *M3* sites, whereas trivalent Fe and Al cations distinctly prefer the more distorted *M4* octahedral site (Bonazzi and Menchetti 1989; Takéuchi and Kogure 1992; Appel and Brigatti 1999; Marincea 2000; Tančić et al. 2012). Tetravalent and pentavalent cations (Ti⁴⁺, Sn⁴⁺, Sb⁵⁺) can replace Fe³⁺ and/or Al³⁺ via Mg(Ti,Sn)⁴⁺(Fe,Al)³⁺_{−2} and Mg₂Sb⁵⁺(Fe,Al)³⁺_{−3} substitutions (Aleksandrov and Troneva 2008) and they probably also occupy the *M4* site. Consequently, a simplified general formula of natural LGM members can be written as X₂YO₂(BO₃), where *X* (*M1*–*M3*) = Mg²⁺, Fe²⁺, Ni²⁺, Mn²⁺ and *Y* (*M4*) = Al³⁺, Fe³⁺, Mn³⁺, V³⁺, Cr³⁺, Sb³⁺, Ti⁴⁺, Sn⁴⁺, Sb⁵⁺, and Mg²⁺ as divalent cation which balances the entry of M⁴⁺ and M⁵⁺ cations (Takéuchi et al. 1950; Bonazzi and Menchetti 1989; Takéuchi and Kogure 1992; Appel and Brigatti 1999; Marincea 1999a).

As indicated by the substitution trends (Figs. 3 and 4), the *M4*-site occupancy of trivalent cations is mostly influenced

Table 5 Representative chemical compositions and calculated mineral formulae of serpentine-group mineral from the Vysoká – Zlatno skarn

Analysis #	R-20D06	R-20D07	R-20D08	R-20D09	R-20D10
Oxide contents measured (in wt%)					
SiO ₂	42.45	41.88	42.12	41.12	41.31
Al ₂ O ₃	0.55	1.18	0.52	0.27	0.77
Cr ₂ O ₃	0.38	0.21	0.29	0.51	0.44
Fe ₂ O ₃	0.00	0.14	1.10	1.82	1.79
FeO	2.10	2.38	0.50	0.00	0.00
MgO	41.43	41.08	42.38	42.86	42.14
H ₂ O (calculated)	12.82	12.80	12.88	12.85	12.80
Total	99.73	99.67	99.78	99.43	99.24
Mineral formulae (in apfu)*					
Si	1.983	1.961	1.961	1.928	1.936
Al <i>T</i>	0.017	0.039	0.028	0.015	0.042
Fe ³⁺ <i>T</i>	0.000	0.000	0.011	0.057	0.022
Sum <i>T</i>	2.000	2.000	2.000	2.000	2.000
Al <i>O</i>	0.013	0.026	0.000	0.000	0.000
Cr	0.014	0.008	0.011	0.019	0.016
Fe ³⁺ <i>O</i>	0.000	0.005	0.017	0.007	0.041
Fe ²⁺	0.082	0.093	0.020	0.000	0.000
Mg	2.886	2.868	2.942	2.996	2.945
Sum <i>O</i>	2.995	3.000	2.990	3.022	3.002
Sum of cations	4.995	5.000	5.000	5.023	5.003
OH	4.000	4.000	4.000	4.000	4.000
O	5.000	5.000	5.000	5.000	5.000

Ti, Mn, Ni, Ca, Sr, Ba, Na, K, F, and Cl contents were below detection limit

*Mineral formulae were calculated based on 9 anions, 4 (OH) anions, 5 cations and valence calculation

by an AlFe^{3+}_{-1} mechanism whereas the $\text{MgTi}^{4+}(\text{Fe,Al})^{3+}_{-2}$ substitution is the dominant mechanism for incorporation of Ti^{4+} into the *M4* site. There was no preference in substituting for Fe^{3+} or Al in the $\text{MgTi}^{4+}(\text{Fe,Al})^{3+}_{-2}$ substitution and this mechanism seems to be independent of AlFe^{3+}_{-1} substitution. Because the *M4* sites are not connected directly but through the *M1-M3* sites (Irwin and Peterson 1999), these are, therefore, transferring charge between two *M4* sites. Nonetheless, there is also no dependence in occupancy of *M1-M3* and *M4* sites; *M1-M3* is solely controlled mainly by the MgFe^{2+}_{-1} substitution.

LGM from the Vysoká – Zlatno skarn show very wide compositional variations and the highest contents of Ti and Al ever reported in this mineral group. Titanium concentrations are up to 17.4 wt% TiO_2 (≤ 0.40 apfu), which corresponds to ≤ 79 mol% of the azoproteite end-member $[\text{Mg}_2(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_2(\text{BO}_3)]$ and Al content reaches 14.4 wt% Al_2O_3 (0.53 apfu), corresponding to 53 mol% of “aluminoludwigite”, an unapproved mineral species of LGM with $\text{Mg}_2\text{AlO}_2(\text{BO}_3)$ end-member formula. Previously reported analyses of LGM have up to 16.5 wt% TiO_2 (76 mol% of azoproteite end-member) from the Dokuchan skarn deposit, Sakha-Yakutia, Russia (Aleksandrov and Troneva 2008) and

up to 12.7 wt% Al_2O_3 from the Korotkovskoe skarn deposit, eastern Transbaikalia, Russia (Kanishchev and Pertsev 1969). Other remarkably elevated concentrations of Ti and/or Al in LGM have been documented from several other skarn occurrences (Aleksandrov 1961; Schaller and Vlisidis 1961; Pertsev and Aleksandrov 1964; Konev et al. 1971; Marinacea 1999b, 2000; Pertsev et al. 2004; Galuskina et al. 2008; Galuskin et al. 2010; Aleksandrov and Troneva 2011).

An Al-dominant borate of the pinakiolite-group with 15.6 to 16.0 wt% Al_2O_3 (~ 0.63 Al apfu), aluminomagnesiophulsite, was described from the magnesian skarn at Kebirin'ya creek, Sakha-Yakutia, Russia (Pertsev et al. 2004). The pinakiolite-group minerals are monoclinic borates with stoichiometry similar to the LGM, but with different crystal structure and characterized by high Sn content (~ 10 to 31 wt% SnO_2 , ~ 0.15 to 0.50 Sn apfu; Pertsev et al. 2004; Aleksandrov 2007; Aleksandrov and Troneva 2008). In contrast, members of LGM are usually poor in tin (< 1 wt% SnO_2 , < 0.01 Sn apfu), Sn-(Ti)-rich ludwigite compositions with ~ 2 –21 wt% SnO_2 (~ 0.02 to 0.29 Sn apfu) are relatively rare, e.g. in Mount Brooks skarns, Alaska, USA (Aleksandrov and Troneva 2008) or Pitkäranta skarn field, Karelia, Russia (Aleksandrov and Troneva 2009). The tin contents in LGM

Table 6 Representative chemical compositions, calculated mineral formulae and mineral fractions of magnetite and spinel from the Vysoká – Zlatno skarn

Mineral Analysis #	Magnetite R-20A36	Magnetite R-20A37	Magnetite R-20D14	Magnetite R-20D51	Magnetite R-20D52	Spinel R-20E42	Spinel R-20E43
Oxide contents measured (in wt%)							
SiO ₂	0.00	0.00	0.19	0.06	0.00	0.08	0.00
TiO ₂	0.00	0.00	0.00	0.00	0.00	0.47	0.54
Al ₂ O ₃	0.00	0.00	0.03	0.00	0.08	64.95	66.52
Cr ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.23	0.27
Fe ₂ O ₃	71.00	70.59	70.89	69.76	70.99	5.32	4.26
FeO	23.71	24.43	22.91	27.39	23.63	0.00	0.00
MnO	0.37	0.30	0.56	0.12	0.33	0.00	0.00
MgO	4.40	3.94	4.99	2.25	4.51	28.57	28.22
Total	99.50	99.26	99.56	99.58	99.54	99.62	99.82
Mineral formulae (in apfu)*							
Si	0.000	0.000	0.007	0.002	0.000	0.002	0.000
Ti	0.000	0.000	0.000	0.000	0.000	0.009	0.010
Al	0.000	0.000	0.001	0.000	0.004	1.861	1.894
Cr	0.000	0.000	0.000	0.000	0.000	0.004	0.005
Fe ³⁺	2.000	2.000	1.985	1.995	1.996	0.097	0.077
Fe ²⁺	0.742	0.769	0.713	0.871	0.738	0.000	0.000
Mn	0.012	0.010	0.018	0.004	0.010	0.000	0.000
Mg	0.246	0.221	0.276	0.128	0.251	1.035	1.016
Sum of cations	3.000	3.000	3.000	3.000	2.999	3.008	3.002
Mg/(Mg + Fe ²⁺)	0.25	0.22	0.28	0.13	0.25	1.00	1.00
Fractions of end members (in mol%)							
Magnetite	74.2	76.9	70.8	86.8	73.9	0.0	0.0
Magnesioferrite	24.6	22.1	27.4	12.8	24.9	4.9	3.9
Jacobsite	1.2	1.0	1.8	0.4	1.0	0.0	0.0
Spinel	0.0	0.0	0.0	0.0	0.2	94.9	95.9
Magnesiochromite	0.0	0.0	0.0	0.0	0.0	0.2	0.3

V, Zn, Ni, and Ca contents were below detection limit

*Mineral formulae were calculated based on 4 oxygen atoms, 3 cations and valence calculation

from the Vysoká – Zlatno skarn are usually negligible; only rarely attain elevated concentrations (≤ 3.2 wt% SnO₂; ≤ 0.04 apfu) which (together with the optical properties) are consistent with the presence of orthorhombic ludwigite and not the monoclinic pinakolite group in the investigated samples. A notable feature is the elevated content of Zr (≤ 1.0 wt% ZrO₂; ≤ 0.02 apfu) in some azoprote and Ti-Al-rich LGM analyses (type 1) from the Vysoká – Zlatno skarn (Table 1). Such an enrichment in Zr has been described only from a skarn aureole around the Tazheran Massif, Baikal area in Russia, where azoprote [≤ 67 mol% of Mg₂(Mg_{0.5}Ti_{0.5})O₂(BO₃) molecule] has ~ 1 wt% ZrO₂ in association with exsolved monocrystal nanorod inclusions of baddeleyite (Galuskin et al. 2010). Similar effective ionic radii (in 10⁻¹⁰ m) of six-fold coordinated Ti⁴⁺ (0.605), Sn⁴⁺ (0.69) and Zr⁴⁺ (0.72) cations (Shannon 1976) enables mutual substitution in the crystal structure of LGM.

Origin of boron

Boron is a typical lithophile element. The greatest concentrations, commonly sufficient for B minerals to form, are found in crustal magmatic and metamorphic rocks, notably B-rich granites, granitic pegmatites and metapelites containing tourmaline-group minerals; stratiform volcano-sedimentary formations (tourmalinites); hydrothermal systems and evaporites, which contain a diverse suite of borate minerals including borax, colemanite and ulexite (e.g., Anovitz and Grew 1996 and references therein). Numerous borate minerals are characteristic phases in some magnesian skarns worldwide, especially along the contact between dolomitic carbonate rocks and intruding magmatic rocks, mainly granitic and syenitic composition (e.g., Marincea 1999a, 1999b; Woodford et al. 2001; Aleksandrov and Troneva 2008, 2009, 2011; Ilinca 2012).

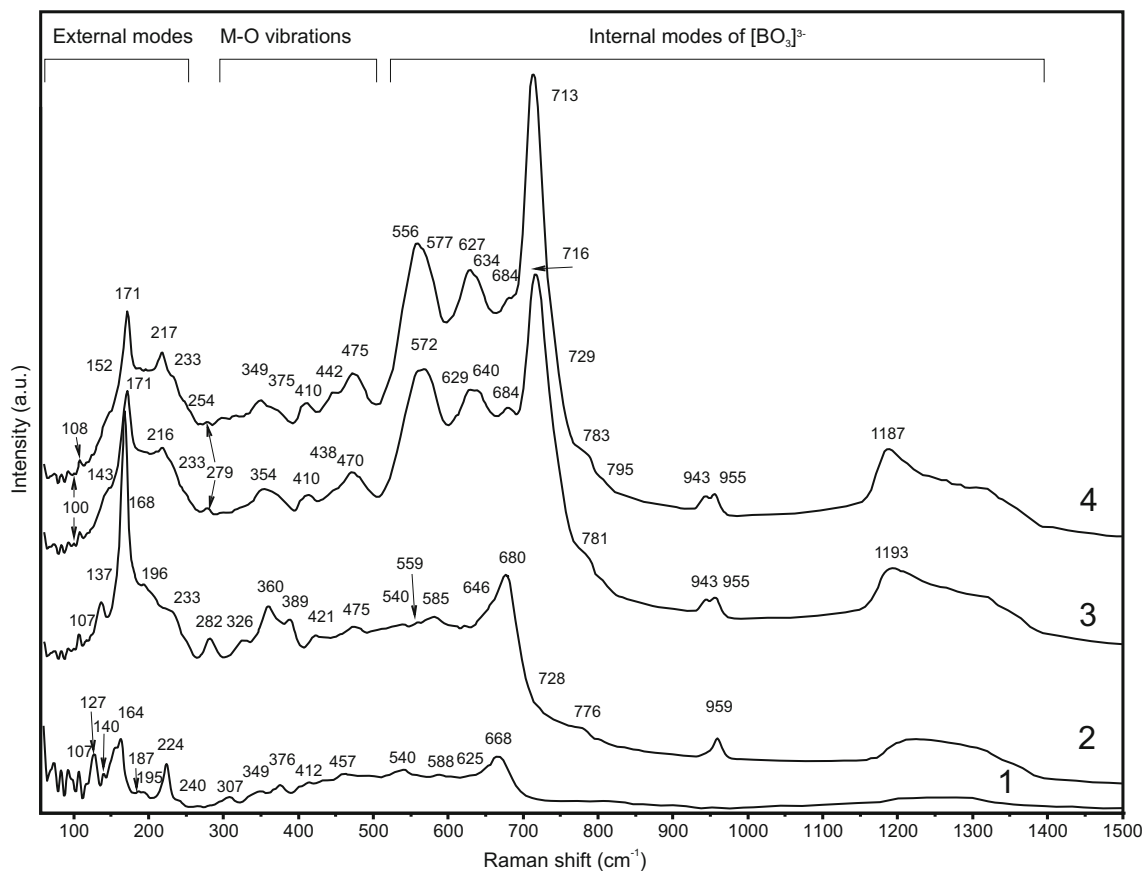


Fig. 6 Raman spectra of various types of LGM from the Vysoká – Zlatno skarn over the 50 to 1500 cm^{-1} spectral range. Spectrum 1: ludwigite of type 4 (Table 1, anal. R-20E41), analogous also to spectrum of ludwigite,

type 3; spectrum 2: Al-rich ludwigite of type 2 (Table 1, anal. R-20E36), spectrum 3: azoproteite of type 1 (0.28 Ti apfu, Table 1, anal. R-20E42), spectrum 4: azoproteite of type 1 (0.35 Ti apfu, Table 1, anal. R-20E43)

Consequently, a question concerning the origin of boron in the borate-bearing magnesian skarns arises: Is boron derived from magmatic to post-magmatic fluids or from an adjacent (meta)sedimentary source? Despite an abundance of data on borate minerals in skarns, most authors have not addressed the source of boron for these minerals. Woodford et al. (2001) assumed a magmatic origin of B in the contact-metamorphic aureole around the Alta pluton, Utah, USA, where fluids emanating from granodiorite to quartz monzodiorite and infiltrating into adjacent magnesian skarn (metamorphosed siliceous dolostone) in episodic pulses could have supplied most of the boron.

Alternatively, boron could be derived from sedimentary rocks of suitable lithologies, adjacent to the magmatic intrusion. For example, layers of lacustrine evaporite sediments in continental volcanoclastic rocks, rich in gypsum or anhydrite, contain borate minerals (e.g., colemanite, howlite, priceite), precipitated during diagenesis of these rocks. Such boron-enriched sediments include large Neogene (Miocene) borate deposits in western Anatolia, Turkey and the Puna plateau, Argentina (Ortí et al. 1998; Helvacı and Alonso 2000). Layers of boron minerals

(boracite, szaibélyite, boracite, congolite, trembathite, etc.) occur also within salt (halite, carnallite, kieserite) and anhydrite-bearing marine evaporite sedimentary sequences, for example at the Penobsquis and Millstream potash salt deposits, New Brunswick, Canada (Grice et al. 2005) or the Kłodawa salt deposit, central Poland (Wachowiak and Toboła 2014).

The biotite-amphibole granodiorite and quartz-diorite porphyry rocks of the Vysoká – Zlatno skarn represent a typical calc-alkaline granitic suite with relatively small to moderate contents of rare lithophile elements, including boron; B concentrations range from 3 to 25 ppm, 5 ppm in average (Marsina 1999). However, locally increased boron concentrations are also known from earlier intrusive phases (mainly granodiorites) of the Štiavnica stratovolcano of Neogene age. Aplite dikes associated with cogenetic granodiorite pluton are distinctly enriched in boron (480 ppm B) with abundant tourmaline of dravite to schorl composition (Demko et al. 2011). Nearly the Vyhne-Klokoč Fe-skarn deposit the Štiavnica granodiorite intrusion has caused local fracturing and brecciation of the Hercynian (Carboniferous) basement granite, where the

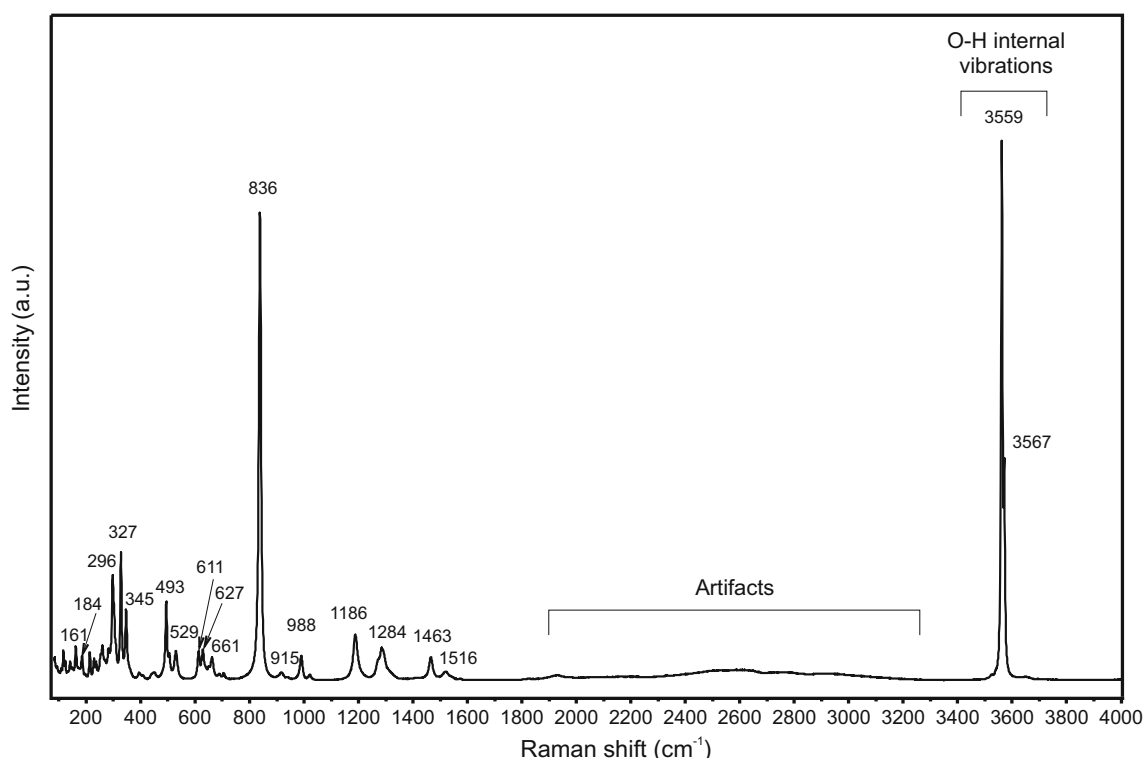


Fig. 7 Raman spectrum of szaibélyite from the Vysoká-Zlatno skarn in the 75 to 4000 cm^{-1} spectral range

fractures are filled by tourmaline and quartz (Koděra et al. 1998). A magmatic source of B is also suggested by tourmaline inclusions in quartz associated with the pyrite-magnetite mineralization hosted by the diorite pluton in contact with the Hercynian basement granite in the NW part of the central zone of the Štiavnica stratovolcano. Disseminated and stockwork mineralization is related here probably to a late-stage skarn process (Koděra et al. 1986).

On the other hand, adjacent dolomitic rocks, which were transformed into skarns along contacts with the intrusive rocks, contain ~60 ppm on average (Marsina 1999). The clastic-evaporite sedimentary sequence of the dolomites with shales, sandstones and up to 20 m thick layers of anhydrite in their upper part belong to the Carpathian Keuper Formation and the Veľký Bok Group of Middle to Upper Triassic age (Koděra et al. 1990, 2010). Therefore, the dolomite and/or anhydrite beds could be also a possible or partial source of boron in the form of diagenetic borates or admixtures in carbonate or sulfate minerals.

Evolution of the skarn mineralization

Aureoles of magnesian skarns are formed at contacts with melts of elevated alkalinity or SiO_2 prior to their consolidation. The supply of Si, Al, and other elements with magmatic fluids causes metasomatic transformation of adjacent dolomite-rich rocks (Woodford et al. 2001; Aleksandrov and Troneva 2008).

Borate mineralization in Mg-skarns is formed during the retrograde stage of metasomatism where kotoite ($\text{Mg}_3\text{B}_2\text{O}_6$) and suanite ($\text{Mg}_2\text{B}_2\text{O}_5$) are common early boron phases, frequently replaced by LGM (e.g., Marincea 1999b; Woodford et al. 2001; Aleksandrov 2007). However, there is no evidence for the presence of kotoite or suanite (even as relicts); instead, only Fe^{3+} -bearing LGM precipitated, possibly due to high $f\text{O}_2$ during the high-temperature stage in the Vysoká – Zlatno skarn. Moreover, the mineral assemblage, textural relationships and variations of chemical composition of the investigated magnesian- and boron-rich skarn minerals indicate a complex evolution in which the following two main stages can be recognized:

- (1) An early high-temperature, contact-metamorphic and metasomatic stage. Interaction of magmatic (granodiorite-related) fluids with a dolomite-shale-anhydrite sedimentary sequence caused precipitation of primary skarn minerals: coarsely-crystalline aggregates of LGM (types 1 to 3), hydroxylclinohumite, Mg-rich magnetite, and rare spinel. Compositional variations in LGM show a sequence of crystallization beginning with the oldest azoprote to intermediate Ti-Al-rich LGM with the highest Ti contents (type 1) and Al-ludwigite to “aluminoludwigite” (type 2), which probably formed probably at a higher temperature, to Ti-(Al)-poor ludwigite compositions of the outer zones (type 3), formed during lower temperature of the contact-metamorphic/metasomatic stage.

- (2) A late retrograde serpentinization and hydrothermal stage. Minerals of this stage form irregular veinlets and aggregates, products of partial alteration of older LGM (types 1 to 3) to szaibélyite and the latest generation of ludwigite veinlets (type 4), as well as the formation of a serpentine-group mineral and clinocllore after hydroxylclinohumite. Moreover, this stage is connected with the precipitation of dolomite, magnesite and sulphide minerals (valleriite, sphalerite, and chalcopyrite). The late retrograde stage, including serpentinization and coeval ore mineralization, was probably governed by low salinity fluids of moderate temperature with fluid inclusion salinities 0–3 wt% NaCl eq. and homogenization temperatures of ~320 to 370 °C (Koděra et al. 2010).

A similarly complex genetic evolution from an early high-temperature stage to a late hydrothermal overprint including several fluid pulses and variations in pH and fO_2 regime has been described from various magnesian skarns (Marincea 1999a; Woodford et al. 2001; Aleksandrov and Troneva 2009, 2011). Ludwigite and “aluminoludwigite” were synthesized over the temperature range of 550 to 700 °C and pressures of 50 to 100 MPa (Bloise and Barrese 2009; Bloise et al. 2010), whereas the thermal stability of szaibélyite is estimated at 200 to 350 °C (Aleksandrov 2008). Based on experimental data, the composition and associated silicate mineral assemblage, temperatures of ~600–650 °C for ludwigite crystallization, and above or near 300 °C for szaibélyite formation during the serpentinization stage are inferred from the Ocna de Fier skarn, Romania (Marincea 1999a). Similar P - T conditions for the borate and associated minerals have also been estimated for the Vysoká – Zlatno magnesian skarn mineralization (700 to <350 °C, 50–70 MPa; Koděra et al. 2010, Uher et al. 2015).

The complex compositional trend of the LGM from early azoprote to Ti-Al-poor ludwigite members (from type 1 to type 4, Fig. 3) and precipitation of szaibélyite records the evolution of the Vysoká – Zlatno magnesian skarn during contact-metamorphic/metasomatic to late hydrothermal stages. Zoned ludwigite crystals with an azoprote core have recently been noted in the Snezhnoye skarn deposit, Russia (Galuskin et al. 2008). However, analogous complex chemical variations have not been reported in LGM until our study. Consequently, such a detailed compositional study of suitable zonal borate minerals (especially LGM) could be a useful tool for understanding of the processes of formation and evolution of boron-bearing skarns.

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