Perovskite, reaction product of a harzburgite with Jurassic– Cretaceous accretionary wedge fluids (Western Carpathians, Slovakia): evidence from the whole-rock and mineral trace element data

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Abstract: Perovskite (Prv) was discovered in an abyssal harzburgite from a "mélange" type blueschist-bearing accretionary wedge of the Western Carpathians (Meliata Unit, Slovakia). Perovskite-1 formation in serpentinized orthopyroxene may be simplified by the mass-balance reaction: Ca₂Si₂O₆ (Ca-pyroxene-member)+2Fe₂TiO₄ (ulvöspinel molecule in spinel)+2H₂O+O₂=2CaTiO₃ (Prv)+2SiO₂+4FeOOH (goethite). Perovskite-2 occurs in a chlorite-rich blackwall zone separating serpentinite and rodingite veins, and in rodingite veins alone. The bulk-rock trace-element patterns suggest negligible differences from visually and microscopically less ("core") to strongly serpentinized harzburgite due to serpentinization and rodingitization: an enrichment in LREE(La,Ce), Cs, ±Ba, U, Nb, Pb, As, Sb, ±Nd and Li in comparison with HREE, Rb and Sr. The U/Pb perovskite ages at ~135 Ma are interpreted to record the interaction of metamorphic fluids with harzburgite blocks in the Neotethyan Meliatic accretionary wedge. Our LA-ICP-MS mineral study provides a complex view on trace element behaviour during the two stages of rodingitization connected with Prv genesis. The positive anomalies of Cs, U, Ta, Pb, As, Sb, Pr and Nd in Cpx, Opx and Ol are combined with the negative anomalies of Rb, Ba, Th, Nb and Sr in these minerals. The similar positive anomalies of Cs, U, Ta, ±Be, As, Sb found in typical serpentinization and rodingitization minerals, with variable contents of La, Ce and Nd, and negative anomalies of Rb, Ba, Th, Nb and Sr suggest involvement of crustal fluids during MP-LP/LT accretionary wedge metamorphism. LA-ICP-MS study revealed strong depletion in LREE from Prv-1 to Prv-2, and a typically negative Eu (and Ti) anomaly for Prv-1, while a positive Eu (and Ti) anomaly for Prv-2. Our multi-element diagram depicts enrichment in U, Nb, La, Ce, As, Sb, Pr, Nd and decreased Rb, Ba, Th, Ta, Pb, Sr, Zr in both Prv generations. In general, both Prv generations are very close to the end-member composition. In spite of low concentrations of isomorphic constituents, Prv-1 and Prv-2 display the ${}^{A}(La,Ce)^{3+} + {}^{B}(Fe,Cr)^{3+} = {}^{A}Ca^{2+} + {}^{B}Ti^{4+}$ heterovalent couple substitution. A decrease of ferric iron in Prv-2 indicates increasing reduction conditions during rodingitization.

Keywords: perovskite, serpentinization, rodingitization, ICP-MS, LA-ICP-MS, Western Carpathians accretionary wedge

Introduction

Perovskite (CaTiO₃) represents an accessory but petrologically important constituent in different lithologies, including: (1) SiO₂-undersaturated, especially alkaline magmatic rocks (Currie 1975; Ulrych et al. 1988; Chakhmouradian & Mitchell 1997, 2000; Mitchell & Chakhmouradian 1998; Heaman et al. 2003); (2) skarns (Marincea et al. 2010; Uher et al. 2011) and (3) in medium to lower-temperature reaction domains in greenschist and blueschist to eclogite facies metamorphic rocks (Müntener & Hermann 1994; Malvoisin et al. 2012).

Mineralogical-petrological data of harzburgite host, and of metamorphic-metasomatic perovskite from the Western Carpathians Meliata Unit (Slovakia), including U/Pb SIMS and LA-ICP-MS perovskite ages and Nd isotopes were published by Putiš et al. (2012, 2014, 2015) and Li et al. (2014).

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Element mobility in accretionary wedges using the LA-ICP-MS data was searched, for example, by Scambelluri et al. (2004, 2014) and Khedr & Arai (2009) in HP peridotites and serpentinites with implications for fluid processes and trace-element recycling. Kodolányi et al. (2012) investigated fluid-rock interaction processes in ocean floor and fore-arc serpentinites.

Our presented data are focused on the origin of the harzburgite host using the mineral (Ol, Opx, Cpx, Spl) chemical composition diagrams. The LA-ICP-MS mineral patterns of Ol, Cpx, Opx, Srp, Grt, Ep and Chl from serpentinized/rodingitized harzburgite domains are compared to the LA-ICP-MS perovskite patterns in their association, documenting a model of perovskite genesis due to hydration processes in an accretionary wedge.

The mineral abbreviations used in text, tables and figures are taken from Whitney & Evans (2010): Act=actinolite, Adr=andradite, Alm=almandine (component), Amp=amphibole (group), Ap=apatite, Atg=antigorite, Chl=chlorite, Cpx=clinopyroxene, Ctl=chrysotile, Czo=clinozoisite, Di=diopside, Ep=epidote, Grs=grossular (component), Grt=garnet, Gth=goethite, Hem=hematite, Hbl=hornblende, Lz=lizardite, Mag=magnetite, Ol=olivine, Opx=orthopyroxene, Prg=pargasite, Pph=pyrophanite; Prp=pyrope (component), Prv=perovskite, Qz=quartz, Spl=spinel, Sps= spessartine (component), Srp=serpentine group minerals, Tlc=talc, Ves=vesuvianite, except for Carb=carbonates.

Geological setting and previous results

Geological setting

The Western Carpathians form a collisional orogenic belt subdivided into Outer, Central and Inner Western Carpathians (OWC, CWC and IWC — Plašienka et al. 1997; Fig. 1); where (1) the OWC are mainly composed of Tertiary flysch complexes, (2) the CWC comprise the basement and Mesozoic cover nappes exposed in the Tatric, Veporic and Gemeric tectonic zones separated by major Late Cretaceous shear zones, and (3), the IWC include Meliata tectonic unit overlain by the Turňa and higher Silica nappes. The underlying Gemeric Unit is composed of mostly low-grade metamorphosed Lower Paleozoic basement complexes with Permian and subordinate Mesozoic cover rocks (Mello et al. 2008). This unit represents the northern or passive continental margin of the Meliata-Hallstatt Ocean. The southern active continental margin in the Inner Western Carpathians is represented by the overlying Turňa Nappe composed of Carboniferous to Jurassic VLT to LT greenschist facies metasediments (Vozárová & Vozár, 1992; Mello et al. 1996). The uppermost tectonostratigraphic unit is composed of Triassic-Jurassic successions of the Silica Nappe (Biely et al. 1996).

The perovskite-bearing serpentinized harzburgite blocks described herein belong to a mélange complex of the Meliata tectonic unit (Putiš et al. 2012). Mock et al. (1998) had previously reported that high-pressure rocks of the Meliata Unit were incorporated in the Bôrka Nappe (Leško & Varga 1980; Mello et al. 1998) overlying the Gemeric and Veporic tectonic units of the CWC, and Faryad (1995) specified metamorphic blueschist facies conditions of 380-460 °C at 9-12 kbar.

The Meliata-Hallstatt Ocean opened in the Anisian-Ladinian time (Kozur 1991), most likely as a back-arc basin (Stampfli 1996). The Late Jurassic closure of this basin was dated at 160–150 Ma by the ⁴⁰Ar/³⁹Ar ages of "phengitic" white mica in the blueschists (Dallmeyer et al. 1996; Faryad



Fig. 1. Geological-tectonic sketch map of the Western Carpathians (after Biely et al. 1996). OWC=Outer Western Carpathians; CWC=Central Western Carpathians, divided into the Tatric, Veporic and Gemeric basement/cover complexes (Late Cretaceous tectonic units) overlain by often less than kilometre-size fragments of the IWC Meliata tectonic Unit. IWC=Inner Western Carpathians.

& Henjes-Kunst 1997). The Meliatic accretionary wedge developed during exhumation of blueschist facies rocks from a subduction channel via a corner flow triggered by the leading edge of the upper plate. This wedge was then transformed between ca. 150 and 130 Ma into numerous small nappe fragments coalescing as the Bôrka Nappe and thrust over the passive continental margin Gemeric and Veporic tectonic units forming the CWC orogenic wedge (Putiš et al. 2014, and citations therein).

Previous results

The Meliatic Bôrka Nappe perovskite-bearing serpentinites associated with blueschists are located in a quarry at Dobšiná town in eastern Slovakia. Radvanec (2009) discovered perovskite in a pale fragment enclosed in serpentinites at the Danková locality, close to Dobšiná and considered that Prv is most likely a product of ultra-high-pressure metamorphism. Putiš et al. (2012) proposed a late-metamorphic origin for Prv related to serpentinization (Prv-1) and rodingitization (Prv-2) of a harzburgite host in a subductionaccretionary wedge, according to geological, mineralogicalpetrological and whole-rock chemical data. A similar type of Prv, mostly replaced by Pph, was described in Perkupa serpentinite in northern Hungary (Zajzon et al. 2013).

Harzburgite was found to be the most abundant ultramafic rock-type in the mélange complex in the Dobšiná quarry; with lherzolites and pyroxenites rarely encountered (Putiš et al. 2012). The mélange complex is composed of decimetreto 100 metre-size fragments of serpentinized harzburgite, talc-"phengite"-glaucophane schists, "phengite" schists, blueschists, metaradiolarites, marbles and their blueschist facies tectonoclastics embedded in a soft serpentinitic matrix. This kind of matrix groups large blocks of HP rocks in olistolith like bodies within the Jurassic anchimetamorphosed turbiditic flysch sediments of the accretionary wedge. The mixture or "mélange" type large composite blocks are formed by (1) subducted high- to medium-pressure metabasalt, metadolerite and metaradiolarite fragments which are the oceanic crust-related (Hovorka et al. 1984), and (2) talc-"phengite" schists and marbles associated with blueschists, the latter most likely related to the subducted (northern) continental margin (Putiš et al. 2014).

The specific position of Prv in serpentinized and rodingitized parts of harzburgite fragments infers a fluid-rock interaction responsible for the occurrence of the two Prv generations. Perovskite-1 formed in serpentinized orthopyroxene (Opx1) porphyroclasts, often accompanied by Adr clusters. Perovskite-2 was found in 1 to 3 cm wide chloriterich blackwall zone separating serpentinite and rodingite veins. Perovskite-2 also occurs in rodingite veins, ingrown by chlorite and apatite, and surrounded by a typical rodingite mineral assemblage of Di, Adr, Ves, Ep/Czo, Ap and Chl. Perovskite is replaced by Pph along the grain rims and interiors. Both Prv generations (mainly Prv-2) are partly to almost totally replaced by (Ti-)Adr (Putiš et al. 2012).

The size, shape and distribution analysis of Prv-1 grains was carried out on drilled cylindrical specimens, 1 cm in diameter (thick 5-10 mm), sampled along a profile of

ca. 20 cm from the dark core to the greenish serpentinized zone of harzburgite, by X-ray micro-tomograph Nanotom 180 at the Institute of Measurement of Science of the Slovak Academy of Sciences in Bratislava. A characteristic X-ray absorption of Prv, besides the other physical properties, such as density and shape, enabled us to visualize the Prv-1 crystal distribution in serpentinite matrix and distinguish them from other silicate, oxide and carbonate minerals (Putiš et al. 2011).

The perovskite location in 200 to 300 μ m thick rock slabs was checked under a polarizing microscope at the Comenius University in Bratislava, and Prv grains, mostly 50 to 300 μ m in size, were then handpicked from the slabs under a stereomicroscope. The perovskite grains were embedded in epoxy and polished to expose the grain-centres (in Beijing). The U/Pb SIMS concordia ages of Prv-1 from 3 samples range from 137±1 Ma to 135±1 Ma, with mean of 135.6±0.58 Ma, while Prv-2 was dated to 133.7±5.4 Ma (Li et al. 2014). Perovskite-1 age at ~135±2.0 Ma was also determined by LA–ICP–MS (Putiš et al. 2015).

The $^{143}\text{Nd}/^{144}\text{Nd}$ mean value of Prv-1 is 0.512153±0.000017 by LA-MC-ICP-MS, thus corresponding to the initial $\epsilon_{\text{Nd}}(\text{t=135})\text{=-}8.2\pm0.4$ (math's mean). This suggests that the subducted and dehydrated continental crust was the main source of the interactive fluids which initiated serpentinization and rodingitization in the Neotethyan Meliatic Jurassic to Cretaceous accretionary wedge (Li et al. 2014; Putiš et al. 2014).

Samples and methods

Sample description

The investigated hand-samples were taken in Dobšiná quarry (N 48°49.622, E 20°21.977) from the central parts of the crushed metre-size serpentinized harzburgite blocks emplaced in a soft serpentinitic matrix.

Partly-preserved magmatic structures of Spl harzburgite were petrographically investigated by Putiš et al. (2012) from the inner Prv-free dark "cores" of serpentinite blocks. These slightly serpentinized dark harzburgitic "cores" consist of Ol (~70 vol. %), Opx1 (~25 vol. %), accessory Spl (~4 vol. %) and rare Cpx1 (~1 vol. %). Magmatically corroded and partly dissolved porphyric Opx1 (±Cpx1) is enclosed in Ol matrix with Spl. Both pyroxenes show exsolution lamellae, of Cpx in Opx1, or Opx in Cpx1, respectively. Aggregates of late-magmatic Cpx2 (~10 vol. %, mostly at the expense of dissolved Opx1) with (~1 vol. %) Cr-Spl, and scarce aggregates of Opx2 with Cpx exsolution lamellae occur at the rim of the Opx1 porphyroclasts. Orthopyroxene1 often forms sygmoidally rotated porphyroclasts, including Срх exsolution lamellae. Microfractures and cleavage planes of the kinked and rotated Opx1 porphyroclasts are filled by Cpx3 (still Al-rich), the latter representing the late-magmatic subsolidus (syn-HT deformation) recrystallization of the Opx1 porphyroclasts. Cloudy lower Al (1.2-2.5 wt. %) Cpx4 and associated Prg occur in metamorphic reaction rims between the Opx1 and Cpx2 aggregates. Central parts of the Cpx2 grains contain exsolution lamellae of Opx, enclosed in metamorphic diopsidic rim (Cpx5, with very low Al_2O_3 contents of 0.02– 0.1 wt. %). The serpentinized harzburgite contains Srp group minerals, Cr-Fe Spl, Prv-1/Pph, (Ti)Adr, Mag and Hem, rarely Carb with Tlc, Qz and characteristic relics of Ol, Opx (with Prv-1), Cpx and Spl. They preserve subsolidus structures with HT-deformed Opx1 and rare Cpx1 porphyroclasts surrounded by late-magmatic aggregate of Cpx2 and Cr-Spl, \pm Opx2.

The pale rodingite veins (1 to 50 cm wide) crosscutting serpentinized harzburgites are composed of Di, Ves, Ep/Czo, (Ti-)Adr, Ap, Chl, Prv-2/Pph. They are separated from serpentinite by a blackwall Chl-rich 1–3 cm across the reaction zone.

Perovskite-1 was discovered in relatively narrow 1 to 20 cm wide zone between a dark "core" and surrounding strongly serpentinized (also Prv-free) zone. Perovskite-1 varies in size from 20 to 700 μ m and it is present in lamellar to cubic shapes or in crystal aggregates within serpentinized Opx porphyroclasts. Perovskite-2 was detected in blackwall chlorite-rich zone separating serpentinite and rodingite, and in rodingite veins alone.

Methods

The major element composition of both Prv generations and X-ray element maps were determined from polished sections by Cameca SX-100 electron microprobe at the State Geological Institute of Dionýz Štúr in Bratislava. Representative chemical analyses of Ol, all Px generations (including those in exsolution lamellae), Spl, Prv, Pph, Adr and Amp from EMPA were published by Putiš et al. (2012, table 1). Additional EMPA Prv analyses are given in Table 1.

The whole-rock major- and a part of the trace elements were determined by X-ray fluorescence spectrometry (XRF) using a PHILIPS PW2400 (Department of Lithospheric Research, Vienna University, Austria). Trace-element (including rare earth elements, REE) contents were analysed by inductively coupled plasma mass spectrometry (ICP-MS) at the Department of General and Analytical Chemistry, Montanuniversity Leoben, Austria. In total 0.1 g of fine grained sample was sintered with sodium peroxide (purity 95 %) to achieve complete digestion of all silicate and spinel mineral phases. Measurements were performed with an Agilent 7500ce ICP-MS collision cell mode with and without He (sample preparation and analytical procedure details in Meisel et al. 2002 and Putiš et al. 2012). These analyses were published by Putiš et al. (2012, table 2) and they are used (Fig. 7) for comparison with the mineral trace element data (Fig. 8).

Perovskite(1 and 2), Ol, Opx, Cpx, Ctl, Grt(Adr), Ep and Chl trace element compositions, including REE, were conducted using the Laser Ablation Multi-collector Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) at the State Key Laboratory of Lithospheric Evolution, Chinese Academy of Sciences in Beijing (China) and The Central European Institute of Technology at Masaryk University in Brno (Czech Republic). Representative trace element analyses of Prv-1 and Prv-2 are in Table 1. The following isotopes were used for determination: ⁷Li, ⁹Be, ²³Na, ²⁴Mg, ²⁷Al, ²⁸Si, ²⁹Si, ³¹P, ³⁹K, ⁴³Ca, ⁴⁵Sc, ⁴⁷Ti, ⁴⁹Ti, ⁵¹V, ⁵²Cr, ⁵³Cr, ⁵⁵Mn, ⁵⁶Fe, ⁵⁹Co, ⁶⁰Ni, ⁶⁶Zn, ⁶⁹Ga, ⁷¹Ga, ⁸⁵Rb, ⁸⁸Sr, ⁸⁹Y, ⁹⁰Zr, ⁹²Zr, ⁹³Nb, ¹⁰⁵Pd, ¹¹⁸Sn, ¹³³Cs, ¹³⁷Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁷Gd, ¹⁵⁹Tb, ¹⁶³Dy, ¹⁶⁵Ho, ¹⁶⁶Er, ¹⁶⁹Tm, ¹⁷²Yb, ¹⁷⁵Lu, ¹⁷⁸Hf, ¹⁸¹Ta, ¹⁸²W, ¹⁹⁵Pt, ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³²Th, ²³⁸U.

Analytical procedures in Beijing approximated those of Yuan et al. (2004) and Xie et al. (2008). Trace element analysis was conducted using an Agilent 7500a ICP-MS. An ArF excimer laser ablation system from Geolas CQ operated at 193 nm with a pulse width of approximately 15 ns was used for laser ablation analysis. Subsequent to 2007 updating of the GeoLas PLUS laser system, 40, 60 µm and larger spot sizes were used, depending on the mineral grain-size. Similar precision was maintained throughout all analyses. The laser repetition rate was 2-10 Hz depending on the signal intensity, with fluency of $\sim 15 \text{ J/cm}^2$. The ablation depth was estimated at ~30-40 µm. With a 40 µm spot size and 4 Hz repetition rate, the ablated material volume was estimated at 200,000 µm³. Helium gas was flushed through the sample cell to minimize aerosol deposition around the ablation pit and to improve transport efficiency (Eggins et al. 1998; Jackson et al. 2004). Trace element concentrations were calculated by using GLITTER 4.0, and these were calibrated with ⁴⁰Ca internal standard and NIST SRM 610 external reference material (Li et al. 2014).

Analytical determination of major and trace elements was performed by means of LA-ICP-MS setup in Brno. This setup consist of laser ablation system UP213 (NewWave, USA) emitting laser pulses with wavelength of 213 nm and pulse width of 4.2 ns and quadrupole ICP-MS Agilent 7500ce (Agilent, Japan). The laser spot with diameter of 40 and 100 μ m were used depending on size of the mineral grains. The rest of ablation parameters such as repetition rate (10Hz) and laser beam fluence (18 J/cm⁻²) were the same for both laser spot sizes. The ablated material was carried from the ablation cell into the ICP-MS by helium with a flow rate of 0.6 l/min. Behind the ablation cell the argon (1.0 l/min) was admixed into the helium flow. The quantification was performed using certified reference material NIST 610 with internal standardization using ²⁸Si.

Results

Origin of harzburgite host

Modal compositions from a few relatively well preserved (weakly serpentinized) samples of ultramafic fragments cores confirmed harzburgite as an original mantle rock. The mineral chemical composition discrimination diagrams (Figs. 2–4) of these samples suggest abyssal peridotites (harzburgites) as precursors of Prv-bearing serpentinites.

Occurrence of perovskite

Perovskite was discovered in abyssal harzburgites from a blueschist-bearing "mélange" type accretionary wedge of

Sample	DO-2DD	DO-2f-1	DO-2f-1	DO-2-3	DO-111	DO-111	DO-111	D0-111		Prv-1	Prv-1	Prv-1	Prv-2	
Mineral	Prv 1	Prv 1	Prv 1	Prv 1	Prv 2	Prv 2	Prv 2	Prv 2		D0-2D	DO-2E	DO-2F	DO-111	
Nb_2O_5	0.04	0.00	0.00	0.00	0.17	0.10	0.10	0.13		n = 6	n = 5	n = 7	n = 4	LDL
TiO_2	55.13	55.60	56.60	55.50	57.71	58.12	56.62	57.96	Sc	lbd	lbd	lbd	16.5	5.000
Cr_2O_3	0.44	0.33	0.29	0.66	0.00	0.00	0.00	0.00	>	80.6	86.9	88.1	495	0.924
La_2O_3	0.46	0.34	0.17	0.31	0.06	0.00	0.05	0.00	Cr	1898	2434	2266	61.0	11.5
Ce_2O_3	1.22	1.08	0.82	1.02	0.28	0.14	0.10	0.25	Ga	1.55	lbd	24.8	1.99	0.540
$\mathrm{Fe_2O_3}$	1.13	1.08	1.17	0.91	0.51	0.34	0.53	0.71	Sr	36.9	56.9	49.4	169	0.100
CaO	39.90	39.41	40.27	39.85	41.30	41.07	40.06	40.89	Υ	477	558	407	239	0.100
$Na_{2}O$	0.00	0.05	0.00	0.04	0.00	0.00	0.03	0.00	Zr	17.8	16.4	0.6	55.9	0.100
Total	98.31	97.89	99.31	98.30	100.03	77.66	97.48	99.94	Nb	144	395	34.9	103	0.100
									Sn	11.5	12.6	16.8	11.7	7.33
Formulae hase	d on 2 cations	3 anions and	l valence calo	ulation					Ba	lpq	lpq	0.3	23.1	0.100
									La	2759	2882	3012	227	0.100
4N	0000	0.000	0000	0000	0 002	0.001	0.001	0.001	Ce	10113	13051	7498	802	0.064
Ë	0.000	0.000	0.000	0.000	0.020	0.003	0.001	0.000	Pr	717	781	835	108	0.100
÷ 1	0.008	0.006	0.005	0.012	0000	0000	0000	00000	Nd	2383	2706	2684	476	0.315
5 -	0.000	0.000	100.0	0.002	00000	00000	00000	00000	Sm	443	516	480	117	0.100
E C	0.004	C00.0	100.0		100.0	0.000	0,000	00000	Eu	102	134	123	21.7	0.108
сс 10.3+	010.0	010.0	0.000	2000	70000		100.0	0.002	Gd	354	410	352	101	0.100
2	07070	0.097	020.0	010.0	1 002	0.000	600.0	0.005	Tb	49.7	60.3	52.0	14.0	0.051
Ca Me	666.0 000 0	196.0	766.0	C66.0	0000	1.000	100.0	0000	Dy	266	309	268	72.5	0.100
Na	000.0	0.002	0.000	200.0	000.0	0.000	100.0	0.000	Ho	44.5	47.7	40.4	13.0	0.100
Sum	600.2	2.004	2.004	600.2	000.2	100.2	7007	7.000	Er	87.0	89.1	75.9	28.6	0.100
5	0101	1 001	1 000	1 000	1 000	1001	1001		Tm	7.45	8.30	6.61	3.49	0.100
Sum A	CIU.I	100.1	1.000	1 000	600.1	100.1	1001	166.0	$\mathbf{Y}\mathbf{b}$	30.2	34.6	25.7	20.2	0.100
Sum B	966.0	1.003	1.004	1.000	166.0	1.000	1.001	1.003	Lu	2.62	2.78	2.21	2.47	0.100
ē		000		000		000		0	Ηf	1.48	1.14	0.75	2.52	0.100
CalliO ₃	98.6	98.8	99.2	98.8	7.66	9.66	9.66	8.66	Ta	lbd	0.7	0.1	8.20	0.057
(Ce,La)FeO ₃	1.0	0.9	0.6	0.7	0.3	0.1	0.1	0.2	Pb	23.0	26.1	13.0	3.15	4.00
(Ce,La)CrO ₃	0.4	0.3	0.2	0.5	0.0	0.0	0.0	0.0	Th	lbd	lbd	lbdl	18.1	0.100
									D	237	299	146	19.8	0.100
Sum A = La+C)e+Ca+Na ∷													
Sum B = Nb+1	1+Cr+Fe								- TDT -	lower detectio	on limit, bdl -	below lower	detection limit	
Ta, Si, Al, Mn,	Ni, Mg, Sr, K	, F, and Cl c	ontents are b	elow detectic	on limit.				Li. Be.	Ni, Co, Ta ar	e helow detec	tion limit		

Table 1: Representative EMPA compositions (in wt. %) and trace elements (in ppm) of Prv-1 and Prv-2 from Dobšiná serpentinite. Average compositions from LA-ICP-MS.

REACTION PRODUCTS OF J/K ACCRETIONARY WEDGE FLUIDS IN W CARPATHIANS

the Meliata Unit in Western Carpathians, Slovakia. The specific position of Prv in serpentinized and rodingitized parts of harzburgite fragments infers a fluid-rock interaction responsible for the two Prv generations. Perovskite-1 formed in serpentinized orthopyroxene (Opx1) porphyroclasts, often accompanied by Adr clusters. A grain scale metasomatic mechanism (Putnis 2009) might have partitioned Ca and Ti from the host Opx1 with Cpx exsolutions (Ca, Ti?), spinel (Ti) and grain-boundary pervasive LREE(Ce,La), Ca²⁺, Ti and Fe³⁺-enriched aqueous fluids to Prv.

Perovskite-1 formation from Ti-bearing spinel and possibly also Ti-bearing Ca-pyroxene member may be simplified by this inferred stoichiometric reaction for the estimated LT/MP-LP conditions: $Ca_2Si_2O_6$ (Ca-pyroxene-member) +2Fe₂TiO₄ (ulvöspinel molecule in spinel)+2H₂O+O₂= 2CaTiO₃ (Prv)+2SiO₂+4FeOOH (goethite). Perovskite-1 exclusively occurs in serpentinized Opx1 porphyroclasts (Fig. 5a) surrounded with characteristic very fine-needle (mostly around 1 µm across) goethite clusters (Fig. 5b). Because of very small grain size, goethite was identified only by EDX analysis, which confirmed iron and oxygen in this phase chemical composition.

Perovskite-1 rarely shows parallel-cube crystal aggregates in Opx1. These growth planes are often parallel to still visible and detectable Cpx exsolution lamellae, most likely (110) plane system of Opx1 (Fig. 5a). However, many Prv grains are obliquely oriented to inferred (110) planes of the host Opx (Fig. 5b, c). Perovskite-1 often shows zoning due to variable content of the LREE(La,Ce) elements (Fig. 5d).

Perovskite-2 occurs in a 1 to 3 cm wide chlorite-rich blackwall zone separating serpentinite and rodingite veins (Fig. 6a). Perovskite-rich veinlets (Fig. 6b), or Prv grain aggregates in Chl-rich matrix (Fig. 6c, d) are characteristic here. Perovskite-2 also occurs in rodingite veins alone, ingrown by Chl and Ap, and surrounded by a typical rodingite mineral assemblage of Di, Ves, Adr, Ep/Czo, Ap and Chl. Perovskite (1 and 2) is replaced by Pph along the grain rims and interiors most likely by fluid-aided coupled dissolutionreprecipitation (Putnis 2009) at increased Fe-Mn element solubility in rodingitization fluids pervading serpentinized harzburgite. Perovskite (mainly Prv-2) is partly to almost totally replaced by (Ti-)Adr (Fig. 6d).

Whole-rock and mineral trace element compositions

Whole-rock trace element composition

We evaluated again our published bulk-rock trace-element patterns from visually and microscopically less altered harzburgite "cores" with the patterns from strongly serpentinized harzburgite (Putiš et al. 2012). Despite macro- and microscopic differences, the obtained Primitive Mantle (PM) normalized patterns are quite unified, suggesting an enrichment in LREE(La,Ce), Cs, ±Ba, U, Nb, Pb, As, Sb, ±Nd and Li in comparison with HREE, Rb and Sr (Fig. 7a, b). The LILE in the core of harzburgite samples display various to relatively high enrichments in Cs and partly Ba besides depleted Rb and Sr. HFSE and REE contents show overall depletions, however Nb is slightly and Sb extremely enriched. Moreover, sample DO 23-core is also significantly enriched in U and Ta. Part of the LILE shows an increase (Cs, Ba and U), but the rest suffered a decrease (Rb, Th and Sr) after serpentinization and/or rodingitization.

Mineral trace element composition

The LA-ICP-MS mineral study provides a complex view of trace element behaviour during the two stages of rodingitization connected with Prv genesis. Hydration of harzburgite was accompanied by trace element, including REE mobility. The PM normalized patterns of Cpx, Opx, Ol from the relic harzburgite "cores" and those of Srp (Ctl), Chl, Ep, (Ti)Adr and Prv from the alteration (serpentinization/rodingitization) domains in harzburgite document strong mobility of LREE, most LILE and some other elements. The positive anomalies of Cs, U, Ta, Pb, As, Sb, Pr and Nd in Cpx, Opx and Ol are combined with the negative anomalies of Rb, Ba, Th, Nb and Sr (Fig. 8a-f). The positive anomalies of the same elements (Cs, U, Ta, Pb, As, Sb, Pr and Nd, including Be in Grt and Ep) in Srp-Ctl, Grt, Ep, Chl and Prv of serpentinites and rodingites, with variable contents of La, Ce, and negative anomalies of Rb, Ba, Th, Nb and Sr (Fig. 8g-p), could suggest involvement of crustal fluids during accretionary wedge metamorphism.

For a comparison, the LA-ICP-MS study revealed strong depletion in LREE from Prv-1 to Prv-2, and typically a positive Eu anomaly for Prv-2 (Fig. 8p). Our multi-element diagram depicts relative enrichment in U, Nb, La, Ce, As, Sb, Pr, Nd, and decreased Rb, Ba, Th, Ta, Pb, Sr, Zr in both Prv generations. Also characteristic seem to be a negative Ti anomaly in Prv-1 and a positive one in Prv-2 (Fig. 8o).

Perovskite from both generations shows a relatively uniform composition. The BSE images illustrate sector zoning of Prv-1 (Fig. 5d) with sectors slightly enriched or depleted in LREE(La,Ce), whereas Prv-2 does not display visible internal zoning. The (unpublished) X-ray element maps of Ca, Fe and Ti are absolutely homogeneous.

In general, both Prv-1 and Prv-2 exhibit negligible admixtures of REE, Fe, Cr and Nb (Table 1). According to EMPA data, the Prv-1 contains 0.2 to 0.5 wt. % La2O3 and 0.8 to 1.2 wt. % Ce_2O_3 , in contrast to only ~0.05 wt. % La_2O_3 and 0.1 to 0.3 wt. % Ce₂O₃ in Prv-2. Similarly, concentrations of Cr and Fe are distinctly higher in Prv-1 in comparison with Prv-2: 0.2 to 0.7 wt. % Cr₂O₃ and 0.6 to 1.3 wt. % Fe₂O₃ in Prv-1, but ≤0.05 wt. % Cr_2O_3 and 0.2 to 0.7 wt. % Fe_2O_3 in Prv-2. On the other hand, Nb content in Prv-1 (≤0.06 wt. % Nb_2O_5) is lower in comparison with Prv-2 (0.1 to 0.2 wt. % Nb₂O₅). Both Prv generations are very close to the end-member composition: Prv-1 encloses 98.7 (rarely 97.2) to 99.2 mol % and Prv-2 shows 99.7 to 99.9 mol % CaTiO₃ (Table 1). In spite of low concentrations of isomorphic constituents, Prv-1 and Prv-2 display the ${}^{A}(La,Ce)^{3+}+{}^{B}(Fe,Cr)^{3+}={}^{A}Ca^{2+}+{}^{B}Ti^{4+}$ heterovalent couple substitution (Fig. 9).

The distribution of REE in both Prv generations, based on the LA-ICP-MS analyses, exhibits a distinctly higher total REE concentration in Prv-1 (14800 to 22800 ppm) in com-



Fig. 2. a — compositional relationship between Fo[=Mg/((Mg+Fe+Ca +Ni)/100) atomic ratio] content of Ol and Cr#[=Cr/(Cr+Al) atomic ratio] of Spl from Dobšiná harzburgites. OSMA (Olivine-Spinel Mantle Array) is a spinel peridotite residual trend (Arai 1994); **b** — discrimination diagram TiO₂ (wt. %) vs. Cr#[=Cr/(Cr+Al)/100 atomic ratio] with plotted Spl from Dobšiná harzburgites (after Franz & Wirth 2000). Melting trend (red curve annotated by melting %) from Choi et al. (2008). FMM - fertile MORB mantle.



Fig. 3. a — The Al₂O₃-TiO₂ (wt. %) diagram of Spl after Kamenetsky et al. (2001) shows a clear relationship of Dobšiná harzburgites to MORB peridotites; **b** — The Cr#[=Cr/(Cr+Al) atomic ratio]-TiO₂ (wt. %) diagram of Spl after Arai (1992) exhibits a similar relationship of Dobšiná harzburgites to abyssal peridotites.

parison with Prv-2 (1200 to 1900 ppm; Table 1, Fig. 8p). Perovskite-1 also shows a strong dominance of LREE over HREE ($La_N/Yb_N=53-101$) in contrast to slightly dominant LREE over HREE or relatively flat REE normalized patterns of Prv-2 ($La_N/Yb_N=2-10$; Fig. 8p). Perovskite-1 reveals slightly to distinctly positive Ce anomaly ($Ce_N/Ce^*_N=1.1-2.2$; Fig. 8o) and a slightly negative Eu anomaly ($Eu_N/Eu^*_N=0.7-1.0$; Fig. 8p), whereas Prv-2 shows a slightly positive Ce anomaly (1.2–1.4; Fig. 8o) and slightly to distinctly positive Eu anomaly (1.2–2.2; Fig. 8p).

Discussion and conclusions

Concerning the genetic aspects, Prv-1 does not occur in relic magmatic mineral assemblages of harzburgite blocks

composed of Ol, Opx, Spl and rare Cpx. Despite Prv-1 can have lamellar-cube shape (Putiš et al. 2011) it was not found as a late magmatic exsolution phase besides Cpx exsolution lamellae in porphyroclastic (deformed) Opx1. In case of considered potential magmatic origin, Prv would have most likely been subjected to dissolution, similar to magmatic Opx1 by the effect of Ca-(Ti) poor aqueous serpentinization fluids, as a potential source of Ca (and Ti) for evolving rodingitization. Perovskite does not belong to HP metamorphic assemblage found only from the relatively well preserved harzburgite "cores". However, these "cores" are good indicators of Prv-1 in a narrow zone between Prv-free "cores" and widely serpentinized (also Prv-free) harzburgite rims (Putiš et al. 2012; Li et al. 2014).

The mineral chemical composition discrimination diagrams (Figs. 2-4) of studied samples suggest abyssal perido-



Fig. 4. a — The Mg#-Al₂O₃ diagram of Cpx and Opx suggests close relationship of Dobšiná harzburgites to abyssal peridotites in diagram of Choi et al. (2008); **b** — Correlation between Dy and Yb in Cpx (after Jean et al. 2010) of harzburgite cores from Dobšiná quarry indicates abyssal peridotites (harzburgites).



Fig. 5. Perovskite-1 images in serpentinized Opx1: \mathbf{a} — two partial cubes of Prv are oriented parallel to relic Cpx exsolution lamellae system; transmitted PL microscope image; \mathbf{b} — Prv surrounded by goethite needles in serpentinized Opx1; transmitted PL microscope image; \mathbf{c} — BSE image of Prv cube obliquely oriented to inferred (110) planes of Opx, with Ctl inclusion; \mathbf{d} — coloured BSE image of zoned Prv showing pale green sectors enriched in LREE(Ce,La) and a red Pph rim.

tites (harzburgites) as precursors of Prv-bearing serpentinites. Low degree (10-12 %) melting of an original abyssal (dry) lherzolite is characteristic. The inferred Opx breakdown/dissolution reaction could be a part of a hypothetical non-stoichiometric reaction proposed by Putiš et al. (2012, E4 event):



Fig. 6. Perovskite-2 in rodingite veins: \mathbf{a} — Rodingite vein with ca. 1cm thick (dark) Prv-rich layer at the contact with serpentinite; \mathbf{b} — Perovskite veinlet in Prv(-Chl) rich layer from a); PL microscope image; \mathbf{c} — BSE image of Prv cubes in Chl aggregate from Prv(-Chl) rich layer; \mathbf{d} — BSE image of Prv and Ti-Adr (a pseudomorph after Prv) in rodingite.



Fig. 7. Primitive Mantle-normalized patterns of harzburgites (normalization according to McDonough & Sun 1995) register the chemical changes from the less serpentinized ("core") to strongly serpentinized parts: \mathbf{a} — the whole-rock trace multi-element patterns; \mathbf{b} — the whole-rock REE patterns (cf. Putiš et al. 2012).

(Mg,Fe,Ca)(Mg,Fe,Al)(Si,Al)₂O₆ (Opx with higher-Ti Cpx exsolution lamellae)+LREE_(La,Ce)-bearing Cpx1-3+(CO₂)_{aq}+ (P,F,Cl,La,Ce)_{aq}+Ca²⁺+Ti⁴⁺ and Fe³⁺=(La,Ce)CaTiO₃ (Prv-1) and/or Ti-rich Adr+Ap+Di+Srp+Carb+Qz.

This reaction was partly modified by Li et al. (2014) to: $(Mg,Fe,Ca)(Mg,Fe,Al)(Si,Al)_2O_6$ (Opx1 with Cpx exsolution lamellae)+ $(La,Ce)_{aq}\pm(CO_2)_{aq}+Ca^{2+}+Ti^{4+}$ and $Fe^{3+}=$ $(La,Ce)CaTiO_3(Prv-1)+(Mg,Fe)_3Si_2O_5(OH)_4(Srp)+Fe_3O_4$ (Mag). They mentioned that Spl was also the source of Ti mobilized by aqueous metamorphic fluids.

Genesis of Prv-1 (Fig. 5) in early rodingitization stage can be defined by this inferred stoichiometric reaction: $Ca_2Si_2O_6$ (Ca-pyroxene-member)+2Fe₂TiO₄ (ulvöspinel molecule in spinel)+2H₂O+O₂= 2CaTiO₃ (Prv)+2SiO₂+4FeOOH (goethite). The reaction could be initiated by influx of H₂O during serpentinization-driven rodingitization. The presence of



Fig. 8. LA-ICP-MS mineral patterns (a-p). Normalization after McDonough & Sun (1995).



Fig. 8 continuation. LA-ICP-MS mineral patterns (a-p). Normalization after McDonough & Sun (1995).

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a Ca-pyroxene member containing Ti might also be inferred according to Cpx exsolution lamellae (with 0.13–0.24 wt. % TiO₂) presence in Opx1 containing only 0.03–0.06 wt. % TiO₂ (Putiš et al. 2012, table 1). Occurrence of Fe-oxides represented by typical needle clusters of goethite around Prv-1 in serpentinized Opx1 is well consistent with this reaction.

The formation of Prv-1 in serpentinized Opx1 (Prv-1 contains inclusions of Srp-Ctl) most likely occurred by grain scale fluid-aided coupled dissolution-reprecipitation mechanism (Putnis 2009; Li et al. 2014). Activities of Ca were likely high, and of Si fairly low, to replace inferred Ca-pyroxene-member and/or Cpx lamellae in Opx1 by Prv-1 at presence of (Ti,Fe)Spl. However, it is not clear, why Prv-1 at presence of (Ti,Fe)Spl. However, it is not clear, why Prv-1 was not found in rare Cpx1 porphyroclasts or Cpx2 aggregates (with an average 0.15 wt.% TiO₂ comparable to Spl) surrounding Opx1. This may have been caused by a less effective dissolution (Ca and Ti release) or a higher Cpx stability and therefore unsuitable nucleation/precipitation (kinetic) conditions for Prv growth in serpentinized harzburgite Cpx that is on the other hand consistent with various (mostly oblique) Prv shape orientation to still recognizable inferred (110) Cpx exsolution lamellae system in serpentinized Opx1 (Putiš et al. 2011).

Perovskite-2 genesis is related to an evolved rodingitization stage. Formation of rodingite veins and veinlets crosscutting serpentinite, where Prv-2 precipitated from rodingitization fluid phase in the form of grain aggregates and veinlets (Fig. 6) followed initial stages of serpentinization. It is remarkable that during an advanced rodingitization stage Cpx was directly (sometimes almost totally) replaced by Adr but not Prv most likely due to distinctly changed redox conditions.

The bulk-rock trace element patterns exhibit relative decrease in REE that can be explained by melt extraction from a harzburgitic residue by a low-degree melting (Fig. 2b). The LREE display a U-shaped pattern (Fig. 7b) mainly due to La and Ce enrichment (Fig. 5d, Table 1). Our samples, enriched in LREE(La,Ce), Cs, ±Ba, U, Nb, Pb, As, Sb, ±Nd and Li in comparison with HREE, Rb and Sr (Fig. 7a, b) can therefore be interpreted as having been overprinted by slab-derived metamorphic fluids (e.g., Scambelluri et al. 2004, 2014; Khedr & Arai 2009; Putiš et al. 2012).



Fig. 9. Substitution diagrams of perovskite from Dobšiná harzburgite serpentinite (Prv analyses from our database).

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Our LA-ICP-MS mineral study revealed behaviour of trace elements during the harzburgite alterations in relationship to Prv genesis. The PM normalized patterns of Ol, Opx, Cpx from the relic harzburgite "cores" and those of Srp (Ctl), (Ti)Adr, Ep, Chl and Prv from the serpentinization/rodingitization domains document many similarities in the positive anomalies of Cs, U, Ta, Pb, As, Sb, Pr and Nd, the negative ones of Rb, Ba, Th, Nb and Sr (Fig. 8a-p), variable contents of La, Ce, suggesting involvement of crustal fluids during accretionary wedge metamorphism. This also highlights the decisive contribution of serpentinization and rodingitization to huge element mobility in the accretionary wedges (e.g., Scambelluri et al. 2014). The obtained Prv LA-ICP-MS patterns, Prv Nd isotopes and the Prv U/Pb isotopic ages (Li et al. 2014) document well a model of Prv genesis due to hydration processes in an accretionary wedge (Putiš et al. 2012, Fig. 8).

The differences in quantity and content of trace elements in the two Prv generations suggest the gradual chemical changes in fluid phase pervading serpentinite. There is typically a distinct decrease in REE content, particularly the LREE by a few orders of magnitude in Prv-2 in comparison with the Prv-1 (Fig. 8o-p), documenting ceasing LREE mobility with changing temperature (decreasing), alkalinity (increasing) and redox (increasing reduction) conditions.

Earlier oxidation conditions during serpentinization are inferred from ferrous iron oxidation in olivine and pyroxene to the ferric iron in magnetite (Müntener & Hermann 1994). Transformation of Prv firstly to Pph indicates still high oxidation potential, but at an increased Fe-Mn mobility in rodingitization fluids. The blueschist fragments could have been a potential source of Fe and Mn during an accretionary wedge late metamorphic-metasomatic event. Transformation of Prv to Ti-Adr and Adr seems to be a marker of a serpentinite redox conditions change (increasing reduction conditions) in Dobšiná rodingites despite the assumption that a part of the ferrous iron from the serpentinite is transferred as ferric iron in Adr (Malvoisin et al. 2012). A decrease of ferric iron in Prv-2 (Fig. 9) is compatible with increasing reduction conditions during rodingitization. This process is well registered in substitution diagrams of both Prv generations (Fig. 9), which are in general very close to the end-member composition. In spite of low concentrations of isomorphic constituents, Prv 1 and 2 display the A (La,Ce)³⁺+ B (Fe,Cr)³⁺= A Ca²⁺+ B Ti⁴⁺ heterovalent couple substitution.

Similar Prv types seem to be suitable constraints of hydration processes in accretionary wedges where eventually a higher quantity of natural (metamorphic-metasomatic) Prv can be expected. The suitable conditions for Prv formation were estimated as temperatures between 400 and 300 °C (according to chlorite thermometer of Cathelineau 1988, applied for Prv-2-Chl intergrowths) at medium to low pressures in the Neotethyan Meliatic accretionary wedge (Putiš et al. 2014, 2015).

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