1. INTRODUCTION

Perovskite has been reported in the following: (1) SiO$_2$-undersaturated magmatic rocks (Currie, 1975; 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 or rodingitization domains in greenschist and blueschist to eclogite facies metamorphic rocks (Müntener & Hermann, 1994; Malvosin et al., 2012).

Although most geochronological publications have focused on magmatic perovskite from kimberlites, lamprophyres, carbonatites, and other alkaline rocks (Heaman, 1989, 2009; Ireland et al., 1990; Simonetti et al., 2008; Frei et al., 2008; Yang et al., 2009; Li et al., 2010; Reguir et al., 2010; Wu et al., 2010, 2013), herein, the U/Pb age of a metamorphic–metasomatic perovskite (Putiš et al., 2012) is determined in the serpentinized zone of the harzburgite by LA–ICP–MS. Perovskite (2) from a rodingite vein was unsuitable for dating by this method because of its very low U content and general high common lead content. The perovskite (1) age is interpreted to record the interaction of metamorphic fluids with harzburgite fragments in the Neotethyan Meliatic accretionary wedge. Since perovskite (1) is younger than the high-pressure metamorphism of this wedge dated at 160–150 Ma, it constrains the exhumation period of the harzburgite fragments at ca. 135 Ma that is compatible with ages of ~137–135 Ma by U/Pb SIMS.

Key words: perovskite U/Pb LA–ICP–MS dating, serpentinization, rodingitization, Meliatic accretionary wedge, Inner Western Carpathians, Slovakia
(1) the OWC are mainly composed of Cenozoic flysch complexes, (2) the CWC comprise the basement and Mesozoic cover nappes exposed in the Tatric, Veporic, and Generic basement-cover complexes (Late Cretaceous tectonic units) overlain by small (often less than kilometer size) fragments of the Meliata tectonic Unit. IWC = Inner Western Carpathians.

The dated Meliatic Bôrka Nappe perovskite-bearing serpentinites associated with blueschist facies rocks are located in the serpentinite quarry at Dobšíná township in eastern Slovakia (Putiš et al. 2011, 2012; Figs 1, 2). Radvanec (2009) discovered perovskite in a pale fragment enclosed in serpentinites at the Danková locality, close to Dobšíná and considered that Prv is most likely a product of ultra-high-pressure metamorphism. Putiš et al. (2012) published geological, mineralogical–petrological, whole-rock chemical data and a preliminary genetic model for perovskite and its harzburgite host. These authors

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

Obr. 1 Geologicko-tektonická skica predkenozoických jednotiek Západných Karpát (podľa Bioľeho et al., 1996). OWC = vonkajšie Západné Karpaty; CWC = centrálne Západné Karpaty, rozdelené na komplexy fundantu a obalu tatrika, veporicka a gmerika (vrchokriedové tektonické jednotky) prekryté príkrovovými fragmentmi meliatskej tektonickej jednotky; IWC = vnútorné Západné Karpaty.

The perovskite-bearing serpentinitized harzburgite blocks described herein belong to a melange 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 Börka Nappe (Leško & Varga 1980; Mello et al., 1998) overlying the Gemenic and Veporic tectonic units of the CWC. Faryad (1995) specified metamorphic blueschist facies conditions of 380–460 °C at 9–12 kbar. Putiš et al. (2012) and Li et al. (2014) estimated temperature of ca. 450–350 °C at high- to medium pressure for the Prv formation.

The melange complex is composed of talc–“phengite”–glau- cophane schists, “phengite” schists, marbles, blueschists of magmatic and sedimentary origin, serpentinites and blueschist facies tectonoclastics (Fig. 2). These occur as decimetre- to 100 metre-size fragments enclosed in a soft serpentinitic matrix, emplaced into Late Jurassic anchimetamorphosed laminated turbiditic flysch sediments.

The Meliata–Hallstatt Ocean opened in Anisian–Ladinian time (Kozur, 1991), most likely as a back-arc basin (Stam- pflü, 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 and 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 (Putiš et al., 2014). It is considered that the Meliatic accretionary wedge was then transformed between ca. 150 and 130 Ma into numerous small nappe fragments coalescing as the Börka Nappe and thrust over the CWC orogenic wedge. This time interval is well documented by K/Ar ages of newly-formed white mica (Árkai et al., 2003) and (U-Th)/He thermochronology (Putiš et al., 2014).

Concerning the genetic aspects, dated Prv (1) does not occur in 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 beside Cpx exsolution lamellae in porphyrolastic Opx. In case of considered potential magmatic origin, Prv would have most likely subjected to dissolution, similar to magmatic Opx, by the effect of Ca-, Ti- (and LREE-Ce,La) – poor aqueous serpentinization fluids, as a potential source of Ca and Ti for evolving rodingitization. Investigated Prv does not belong to HP metamorphic assemblage, the latter registered exclusively from the harzburgite “cores”. However, the “cores” are good indicator of Prv (1) in neighbouring narrow zone between Prv-free “cores” and serpentinitized harzburgite rims (Putiš et al., 2012; Li et al., 2014). It is interesting that rare Cpx, porphyroclasts and Cpx, aggregates in harzburgites, or Cpx-rich aggregates in rare lherzolites and clinopyroxenites were much more resistant to serpentinization, what explains missing Prv in these hydrated rocks. Clinopyroxene exsolution lamellae in Opx, porphyroclasts of a harzburgite could have been source of Ca and Ti in dissolving Opx, for ingrowing Prv (1). Clinopyroxene became a source of Ca and Ti in an advanced rodingitization stage by the effect of CO2-rich aqueous fluids, however not for Prv, but directly for (Ti-) Adr crystallization. The best evidence of this process is pseudomorphic replacement of Prv and/or Cpx by Adr aggregates in rare lherzolites and pyroxenites.

Major element compositions of dated Prv were obtained from polished sections using a Cameca SX-100 electron microprobe at...
the State Geological Institute of Dionýz Štúr in Bratislava (Putiš et al., 2012). Perovskite trace elements detected by LA–ICP–MS are reported by Li et al. (2014). LA–ICP–MS analysis for U/Pb age determination was used also in this paper.

3. MATERIAL AND METHODS

Over 100 grains of perovskite (1) was separated from sample DO-2 Opx porphyroclasts in serpentinized parts of harzburgite fragments (Fig. 3a,b). Perovskite-free dark “cores”, with well-preserved original magmatic structures of Sp harzburgite in the serpentinites, were discarded. Perovskite (1) varies in size from 20 to 700 µm and it is present in either lamellar to cubic shape or in crystal aggregates. Meanwhile, Prv (2) was recovered from rodingite veins crosscutting the serpentinites (Fig. 3c,d).

Perovskite presence in our 200 to 300 µm thick rock-slab samples was checked under a Leica DM2500 P microscope at the Comenius University in Bratislava. Perovskite (1) grains, mostly 50 to 300 µm in size, were then handpicked from the samples under a stereomicroscope, embedded in epoxy and polished to expose grain centres.

Perovskites from the Dobšiná serpentinized harzburgites were cast in each epoxy mount with the perovskite Afrikanda (AFK) and Tazheran (TAZ) standards. The ellipsoidal spot was ca. 20 × 30 µm in size and this produced 30–40 µm ablation depths.

U/Pb ages were determined by LA–ICP–MS at the State Key Laboratory of Lithospheric Evolution at the Chinese Academy of Sciences in Beijing, employing analytical procedures from Yuan et al. (2004) and Xie et al. (2008). An ArF excimer Geolas CQ system operating at 193 nm with a pulse width of approximately 15 ns was used in laser ablation analysis. Subsequently, 40, 60 µm and larger spot sizes were used in the 2007 updated GeoLas PLUS laser system. This choice depended on the mineral grain-size, and precision was meticulously maintained throughout this procedure. The laser repetition rate was 2–10 Hz depending on signal intensity, with fluency

![Microphotographs of perovskite](image-url)
of ~15 J·cm⁻², with ablation depth estimated at ~30–40 μm. With a 40 μm spot size and 4 Hz repetition rate, the volume of ablated material was approximately 200,000 μm³. Helium gas was then 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). The flow rate of He is usually ca. 0.85 L·min⁻¹.

U/Pb analysis was conducted by Agilent 7500a ICP–MS. During laser ablation, the sensitivity of ²³⁸U using NIST SRM 610 standard glass at 40 μm spot and 10 Hz repetition rate was 14,000 cps/ppm. The mass stability was greater than 0.05 amu/24 h; and the ICP–MS detector’s Pulse/Analogy (P/A) was corrected prior to routine analysis. A tuning solution optimized instrumental parameters to ensure oxide CeO⁺/Ce⁺ and doubly charged Ce⁺⁺/Ce⁺ productivity less than 0.5% and 3%, respectively; and also ⁸⁹Y sensitivity greater than 20 × 10⁶ cps/ppm. The background ²³⁴Pb and ²⁰⁴Hg were less than 50 cps resulting from the high purity of employed argon and helium gas.

LA–ICP–MS measurements were performed using time-resolved analysis and peak hopping at one point per mass. The dwell time for each isotope was set at 6 ms for Si, Ca, Ti, Rb, Sr, Ba, Nb, Ta, Zr, Hf and R.E.E., 15 ms for ²⁰⁸Pb, ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁹Pb and 10 ms for ²³⁸Th and ²³⁴U. Each 5 sample analysis was followed by one Afrikanda (AFK), Tazheran (TAZ) perovskite and NIST SRM 610 measurement, and each spot analysis consisted of approximately 30 s background and 60 s sample data acquisition. The ²⁰⁷Pb/²³⁵U, ²⁰⁶Pb/²³⁸U, ²⁰⁷Pb/²³⁸U (²³⁸U/²³⁵U = 137.88) and ²⁰⁸Pb/²³⁵Th ratios were corrected with IR as external standard. Isotope fractionation was corrected and results were calculated by GLITTER 4.0 (GEMOC, Macquarie University; van Achterbergh et al., 2001), and all measured isotope ratios of standard IR (Ice River) perovskite were regressed during sample analysis and corrected using recommended values, with standard deviations set at 2%. The two stage ²⁰⁷Pb model (Stacey & Kramers, 1975) was applied to make common Pb isotopic ratio corrections (see also Williams, 1998), and the ²⁰⁶Pb/²³⁵U weighted mean ages were calculated by ISOPLOT 3.0 (Ludwig, 2003). While individual analysis errors based on counting statistics are at the 1σ level, errors on the pooled ages are quoted at 2σ or 95% confidence level. Trace element concentrations were calculated using GLITTER 4.0 and calibrated using ⁶⁰Ca as the internal standard and NIST SRM 610 as external reference. Analytical uncertainties were mostly within 10%.

4. RESULTS

4.1. In situ LA–ICP–MS analysis of perovskite AFK and TAZ standards for U/Pb dating

AFK perovskite was dated by Wu et al. (2013) from Kola Peninsula alkaline complex. The perovskite U–Pb ages are 377±5 (pyroxenite), 379±2 to 385±5 (calcite-bearing perovskite ore) and 376±5 (ijolite–melteigite) Ma, indicating that this complex formed at ~380 Ma.

Tazheran perovskite from the skarn deposit in the Lake Baikal area of eastern Siberia is used as the U–Pb standard for the Sensitive High Resolution Ion Microprobe (SHRIMP) analysis at Curtin University in Western Australia. Although its chemical composition is unavailable, previous Thermal Ionization Mass Spectrometry (TIMS) analysis indicated that its ²⁰⁶Pb/²³⁸U ratio of 0.074465 provides a concordia age of 463 Ma (Kinny et al., 1997). Tazheran perovskite has unusually high U content in excess of 1000 ppm, and chemical analysis highlighted that it consists of relatively pure CaTiO₃, with minor amounts of Nb, Fe⁺⁺ and REE (Ireland et al., 1990; Yang et al., 2009). It has approximately 10 ppm common Pb, with ²⁰⁶Pb/²³⁸U ratio ranging from 250 to 1000 (Oversby & Ringwood, 1981; Ireland et al., 1990; Kinny et al., 1997). The Isotope Dilution–Thermal Ionization Mass Spectrometry (ID-TIMS) determined TAZ perovskite age at 463 Ma, and its 0.074465 ²⁰⁶Pb/²³⁸U ratio is used to standardize SHRIMP measurements (Oversby & Ringwood, 1981; Ireland et al., 1990; Smith et al., 1994; Kinny et al., 1997). However, Kinny et al. (1997) reported that TAZ perovskite has highly variable U and Th concentrations, even within single grains, thus rendering it unsuitable as a concentration standard.

11 U/Pb analyses were conducted on AFK and TAZ standards, respectively, and weighted ²⁰⁶Pb/²³⁸U ages of 388.1±5.3 Ma (AFK) and 467.4±5.6 Ma (TAZ) were recorded when the ²⁰⁷Pb correction method was implemented (Fig. 4a–b). These ages are identical, within error, to the recommended values of measured standards.

4.2. Perovskite (1) LA–ICP–MS U/Pb dating

Perovskite (1) from the DO-2 serpentinitized harzburgite sample is euhedral, 20–700 μm across, and exhibits almost no alteration. Examples of DO-2 Prv (1) spots dated by LA–ICP–MS are depicted in Fig. 4c. The highest quality crystals were used to measure spots, thus eliminating fractures and inclusions such as Srp, and Ni, Fe, S phases, and also Pph and Adr replacement domains.

Ten DO-2 sample Prv (1) grains (Fig. 4c) from the Dobšiná serpentinitized harzburgite were selected for LA–ICP–MS analysis, with twenty-six spots analyzed for U/Pb age determination (Tab. 1). These have high U and Th concentrations and low common Pb concentrations. The ten perovskites have an age of approximately 134.8±2.1 Ma on the concordia Tera-Wasserburg diagram, compatible with a ²⁰⁷Pb corrected age of 135.2±2 Ma (Fig. 4d).

5. DISCUSSION

The perovskite (1) generation from Dobšiná has very low Th concentration and Th/U ratio; very different to magmatic (e.g., Wu et al., 2010) and other reaction–metasomatic (e.g., Yang et al., 2009) perovskites. However, its common Pb is also very low, thus rendering it suitable for precise U/Pb LA–ICP–MS dating. Perovskite (2) grains in DO-111 sample of the Dobšiná rodingites have lower U and Th concentrations and mostly higher common Pb concentrations than Prv (1). It also has variable Th concentrations and Th/U ratios, thus rendering it unsuitable for precise dating.
The Prv (1) age of ca. 135±2 Ma from LA–ICP–MS analysis is consistent with the inferred post-magmatic, metamorphic–metasomatic origin of Prv bound to serpentinization and/or rodingitization in a subduction-related accretionary wedge (Putiš et al., 2012; Li et al., 2014).

The obtained LA–ICP–MS U/Pb age of Prv (1) is compatible with the U/Pb SIMS ages (from 137±1 Ma to 135±1 Ma, with a mean age of 135.6±0.58 Ma) of the same Prv generation in the Dobšiná Quarry (Li et al., 2014), pointing a suitability of the LA–ICP–MS dating also of this specific metamorphic–metasomatic type of perovskite, first time dated by this method. This age falls into an interval of K/Ar ages of newly-formed white mica dated from this accretionary wedge (Árkai et al., 2003). This age is well consistent also with the low-temperature (U-Th)/He thermochronology reported from this wedge (Putiš et al., 2014).

The Prv (2) age is considered younger because of slightly postponed rodingitization compared to serpentinization; and this is confirmed by petrographic study.

The perovskite (1) age is younger than the 160–150 Ma for “phengitic” white mica from the associated high-pressure rocks of blueschist facies (Dallmeyer et al., 1996). Since Prv is exclusively present in serpentinized and rodingitized harzburgite, the obtained age of approximately 135 Ma indicates concurrent fluid interaction with harzburgite fragments in the accretionary wedge during exhumation-related serpentinization/rodingitization. This date also constrains the earliest Meliatic Nappe
overthrusting the CWC orogenic wedge (e.g., Putiš et al., 2009 and references therein).

6. CONCLUSIONS

Very low Th concentration, low Th/U ratios and generally low common lead content make Prv (1) suitable for precise in situ LA–ICP–MS dating. Moreover, the exactness of this method approaches the U/Pb SIMS results.

The Tera-Wasserburg age of Prv (1) at 134.8±2.1 Ma (and 207Pb corrected age of 135.2±2 Ma) obtained by U/Pb LA–ICP–MS dates the interaction of slab- and accretionary wedge-derived serpentinization/rodingitization fluids with harzburgite blocks during their exhumation from a subduction channel and incorporation in accretionary wedge.

The obtained Early Cretaceous age constrains the earliest age of the Meliatic Bôrka Nappe overthrusting the CWC orogenic wedge.

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7. REFERENCES


