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Short communication

Re–Os isotopic constraints on the source of platinum-group minerals (PGMs) from the Vestřev pyrope-rich garnet placer deposit, Bohemian Massif

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ABSTRACT

Mineralogical studies of the heavy fraction from a Holocene pyrope-rich garnet placer deposit at Vestřev (Krkonoše Piedmont Basin, Bohemian Massif) have identified the presence of very rare grains of platinum group minerals (PGM). Pt–Fe alloy grains are accompanied by Os–Ir–Ru minerals (native osmium, iridium, and ruthenium) with inclusions of Pt–Fe alloy and hongshiite (PtCu). This mineral assemblage is typical for several mantle settings including ophiolites. The chemistry of the Os–Ir–Ru minerals shows an enrichment of the PGM in Ru, which is typical of ophiolites. The grain morphology of PGM and pyrope-rich garnet (mostly rounded with numerous euhedral/subhedral grains) does not exclude a common source. In-situ laser-ablation MC-ICP-MS was used to measure the Re–Os isotopic compositions of single Os-rich grains, which show heterogeneous subchondritic Os isotopic compositions (^{187}Os/^{188}Os = 0.12082–0.12505 ± 0.00003). This precludes their low-temperature origin and indicates derivation of platinum-group elements (PGEs) essentially from mantle-derived rocks without a significant contribution of crustal Os. The mantle model age (T_{MA}) and Re-depletion model age (T_{RD}) model ages range from ~0.4 to ~1.0 Ga and most likely reflect a long history of melt depletion that affected the mantle sources of PGM.

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1. Introduction

Platinum group minerals (PGMs) have been reported from many different placers around the world (e.g., Cox and Singer, 1986). Placers in the former USSR and Colombia, and to a lesser extent in Canada, were the principal sources of the PGEs up to the first quarter of the 20th century, when primary deposits were discovered in South Africa and Siberia (Hattori and Cabri, 1992). Derivation of PGM nuggets from ultramafic rocks by weathering and mechanical processes of transportation (e.g., Betekhtin, 1961), low-temperature formation of PGM nuggets in lateritic soils (e.g., Augustithis, 1965; Augé and Legendre, 1994; Traoré et al., 2006) and crystallization of PGM minerals in placers (e.g., Bowles, 1988) represent the major mechanisms suggested for their origin.

Besides classical mineralogical and morphological studies (e.g., Zientek et al., 1992; Weiser and Bachmann, 1999; Cabri et al., 1996; Tolstykh et al., 2002a; Barkov et al., 2005; Johan, 2006 and references therein) in-situ Os-isotope analyses have proved to be very useful in the identification of the reservoirs from which PGMs are derived (e.g., Hattori and Cabri, 1992; Lyon et al., 1997; Malitch, 2004; Malitch and Merkle, 2004; Malitch et al., 2002; Malitch and Thalhammer, 2002; González-Jiménez et al., 2012 and others).

On the territory of the Bohemian Massif, the only placer historically containing native Pt (up to 42 g/t) was reported by Löw (1928) in the northern part of Bohemia at Tolštejn (Lugikum). However, later attempts to confirm PGMs at this site have not been successful. Several placer deposits exploiting pyrope-rich garnet have been known. The largest, and the only one currently mined, is located in Podsedice, České Středohoří Mts (Fig. 1). Seifert and Vrána (2005) suggested that pyrope-rich garnet has been primarily derived from garnet peridotites that were tectonically emplaced in a shallow subsurface position in the upper crust, directly below sediments of the platform cover. During the platform evolution of the area, these rocks underwent strong weathering and garnets were first deposited in Permo-Carboniferous beds and later re-deposited in Cretaceous sediments before their final concentration in Quaternary alluvial sediments. To date, the only place with identified PGMs from alluvial sediments in the Bohemian Massif remains a Holocene alluvial placer which was mined for pyrope-rich garnet at Vestřev.

Our study brings new data on PGM from the pyrope-bearing placer at Vestřev and uses detailed mineralogical, geochemical and in-situ Os-isotope studies to provide new insights into the mechanism of

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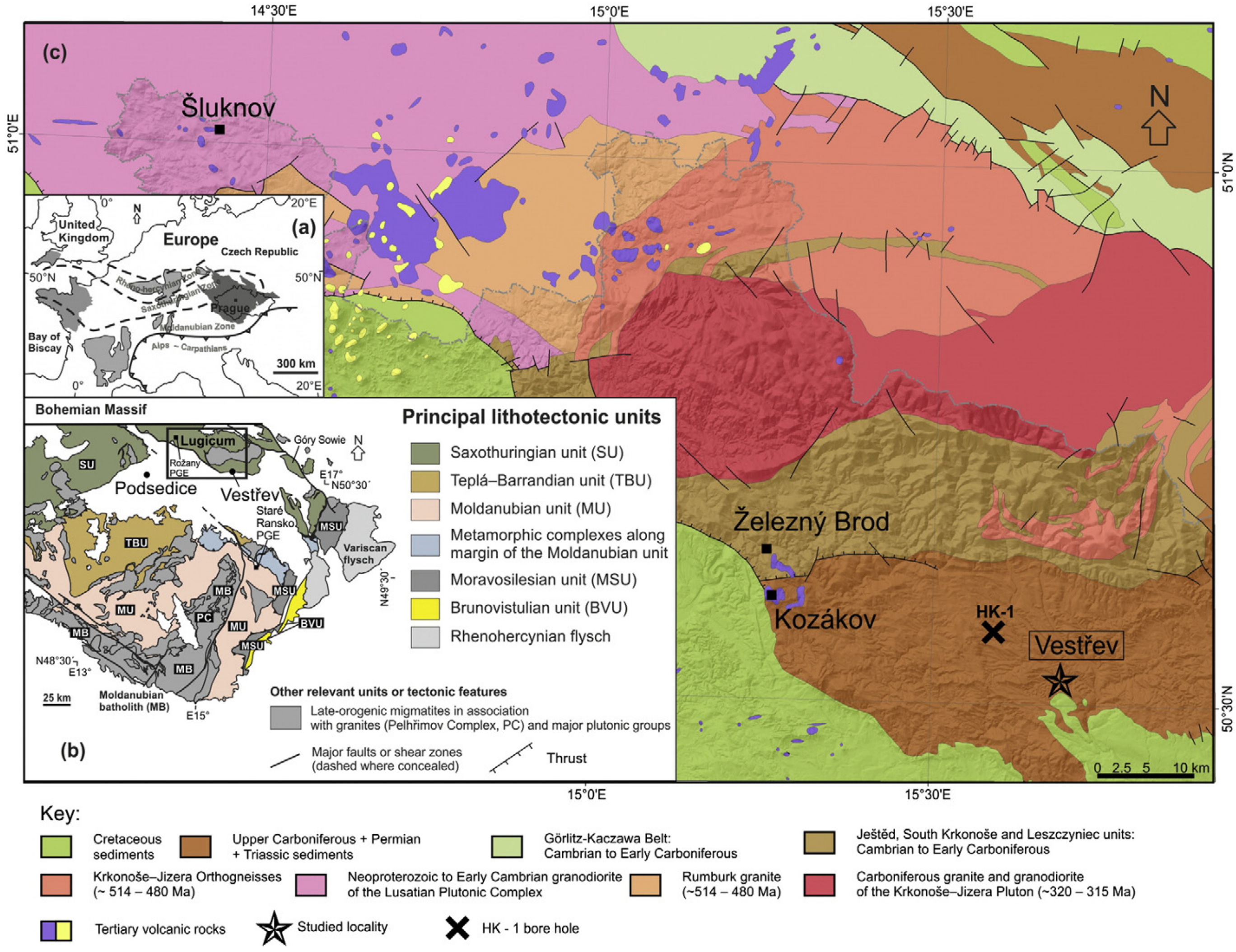

Fig. 1. Simplified geological map of the area of the Vestřev placer deposit with its position within the European Variscides. Adapted from Cháb et al. (2010) and Trubač et al. (2014).

formation of PGMs, their source and their relationship to major tectonomagmatic events in the geological history of the Bohemian Massif.

2. Geological setting and placer deposit

2.1. Regional geology

The basement rocks of the Bohemian Massif represent a remnant of the Variscan orogenic belt spread across Western to Eastern Europe. The orogen itself is divided into seven linear tectonic units or belts between the Rhine area in the north and the Danube region to the south (Franke, 1989; Matte, 2001; Cháb et al., 2010 and others).

The pyrope-rich garnet placer deposit at Vestřev is geologically situated in the Lugicum belt, which represents a mosaic of crustal domains composed of various sized blocks (units). The Lugicum is also known as the Western Sudetes (West Sudetic Belt, Zone) (Cháb et al., 2010). The present erosional level reveals a wide variety of rock types brought together by orogenic processes: Neoproterozoic and Cambrian to Ordovician basement, Cambrian to Lower Carboniferous marine and terrestrial basin fills, very low-grade metamorphosed or completely unmetamorphosed rocks, and gneisses and migmatites with slices and boudins of granulite, eclogite, and peridotite (e.g., Sowie Góry or Orlice-Sněžník blocks).

The allochtonous domain in the Lugicum is represented by a group of nappes that were moved towards the NW from a root zone between the Saxothuringian and Teplá-Barrandian microplates. The lithology and scales of individual nappes are very different. Besides relics of oceanic crust in both the Železný Brod and Rýchory Complexes (protoliths of bimodal volcanogenic rocks were dated by U–Pb at 515–480 Ma; Bendl and Patočka, 1995; Kryza and Pin, 1997; Timmermann et al., 2000) and ophiolites at the border of the Sowie Góry (dated at 420–400 Ma; Oliver et al., 1993; Zelazniewicz et al., 1998) they also comprise volcano-sedimentary sequences. These were formed in the deeper parts of the Saxothuringian continental slope and in oceanic basins during Lower Paleozoic rifting, probably starting during the Ordovician (Kachlík and Patočka, 1998; Patočka et al., 2000; Dostál et al., 2001). Mafic and ultramafic rocks in this area, which were squeezed between the Barrandian and Saxothuringian terranes and may be part of the Teplá terrane (Matte et al., 1990), are considered to represent ophiolitic sequences (Kastl and Tonika, 1984).

Subduction of oceanic crust and crustal segments ceased at about 360 Ma (Maluski and Patočka, 1997). This subduction was followed by exhumation of deeply-subducted crustal fragments and their movement to para-autochtonous and autochtonous units in the fore-deep of deformation front, at about 345–324 Ma (Marheine et al., 2002).

2.2. The placer deposit at Vestřev

The pyrope-garnet placer at Vestřev is located ca 3 km south of Hostinné (East Bohemia) in the Holocene alluvium of the Kalenský

(Olešnický) brook (Fig. 1). The drainage area of this brook consists mainly of lower Permian sediments dominant over volcanic rocks and relics of Cenomanian sandstone and Neogene fluvial gravel (Prouza and Tásler, 2001).

The placer deposit was discovered during exploration work carried out by the Czech Geological Survey in the period 1986–1988 (Žežulka, 1989) and pyrope garnet was exploited from 1994 to 2009. Accumulations of pyrope-rich garnet were restricted to a ~0.1–2.5 m thick layer developed in the lower part of the alluvial deposit; it is composed of Holocene clay-rich gravel containing abundant rock pebbles and fragments and sandy gravel. The garnet-bearing layer showed a sharp hanging-wall contact and its graded bedding clearly showed that the deposit was formed during one large sheet flood. Locally, "pockets" rich in heavy minerals were formed in the footwall, a red-brownish feldspathic čistecký sandstone of Cisuralian age (295–275 Ma), which locally contains clay-rich layers. Two-thirds of the pebbles in the garnet-bearing layer were rocks of the South and East Krkonoše Complex of Neoproterozoic age (e.g., phyllite and quartz), most likely derived from Tertiary terraces of the Elbe river, whose relics are known from the area NNW of Vestřev. The remaining fragments consist of Permian aleuropelite and melaphyre (a dark igneous porphyry embedded with feldspar crystals) and chalcedony, jasper and rarely petrified wood.

Based on exploitation results, the content of heavy minerals in the productive layer was estimated at 2 kg/m^3. The heavy concentrate consisted mainly of hematite and less limonite with about 10% of pyrope-rich garnet. Goethite, almandine, rutile, magnetite, tourmaline, monazite, cassiterite, zircon, apatite, titanomagnetite, ilmenite, leucoxene and barite were the main accessory minerals. Rarely, goyazite, svanbergite, kemlitzite, amphibole, pyroxene, staurolite, corundum (sapphire), spinel, native gold and silver were identified (Moravec and Pauliš, 1997; Moravec, 2002). Anthropogenic contamination may be represented by individual grains of metal alloys (Au–Sn, Cu–Sn–Zn, Pb–Cu–Sn and Fe–Cr–Ni). Unfortunately, there are no geochronological data available from either monazite or zircon.

Red-brownish čistecký sandstone (Cisuralian age) is the host rock for pyrope-rich garnet and the majority of other heavy minerals, but their primary ultramafic source rocks do not outcrop. It is very likely that the alluvial and Permian sediments are underlain by volcanogenic rocks of the Železný Brod Complex (Cambro-Ordovician oceanic-crust type rocks). A completely buried mafic body situated within the phyllite and mica schist basement is considered to be the main cause of the high gravity in the area of the Late Paleozoic Krkonoše Piedmont Basin (Sedlák et al., 2007). This hidden mafic body was interpreted to reach a depth of 5 to 6 km beneath the current surface near the town of Vrchlabí (Sedlák et al., 2007). In 1989, the deep HK-1 (Horní Kalná) borehole was drilled to verify the extent of Permo-Carboniferous sediments (not the character of gravimetric anomaly), Fig. 1. At a depth of 1384 m, below Permo-Carboniferous sediments, a 99.8 m sequence of medium- to coarse-grained amphibolitic gabbro with layers of strongly recrystallized metabasites up to 10 m thick, and veins of trondhjemite (up to several tens of cm thick) was encountered (Chaloupský, 1989). Chaloupský (1989) noted that this intrusive rock complex cannot be compared to any other rocks known in the neighboring Krkonoše unit and suggested that it is a part of the Teplá-Barrandian unit which continues under Permo-Carboniferous and Cretaceous sedimentary cover into East Bohemia. The question remains whether this complex can represent a Meso/Neoproterozoic intrusion or if it was related to early Paleozoic rifting.

3. Samples and analytical methods

3.1. Samples

The study of fine-grained heavy fraction of waste material after exploitation of the pyrope-rich garnet at Vestřev resulted in the identification of native gold (grains usually <1 mm). It is difficult to quantify the gold content in the waste material as it was not systematically studied, but it can be estimated at several tens of mg/m^3, which is far from being economically significant. Seven steel-gray grains of PGM (ranging from 230 to 800 μm in diameter) were discovered only accidently during cleaning of the "gold-rich" concentrate; we used all seven grains for detailed optical and in-situ LA-ICP-MS study. According to Malec and Böhmová (2012) native Pt containing 6–8 wt.% Fe, often also up to 1 wt.% Rh and 0.5 wt.% Cu, is more abundant than Os–Ir–Ru phases. Unfortunately, we did not have any of them available for more detailed study, and thus refer to what was briefly published in Czech with English abstracts.

3.2. Analytical methods

We used reflected-light optical microscopy, and Energy Dispersive (EDS) X-ray spectra on a Link 860/2 electron microprobe in the former Institute of Raw Materials (Kutná Hora, Czech Republic) for the identification of PGM grains. Back-scattered-electron images were taken of each grain using a Scanning Electron Microscope (SEM — CamSc an 3200) at the Electron Microprobe Laboratory of the Czech Geological Survey (Prague, Czech Republic). The grains were later analyzed by electron microprobe at the Institute of Geology, Academy of Sciences of the Czech Republic (Prague, Czech Republic) using a CAMECA SX100 instrument, under the following operating conditions: accelerating voltage 15 kV, sample current 10 nA and beam diameter 2 μm. The X-ray lines measured were OsMα, IrMβ, RuLα, PtMα, FeKα, and CuKα for Os–Ir–Ru–Fe alloys and hongshiite (Pt–Cu) and PtMβ, FeKα, RhLα, and IrMα for platinum. Pure metals were used as standards for Os, Ir, Ru, Rh, and Pt, and magnetite for Fe and cuprite for Cu. The interferences IrLα!CuKα, RuLβ! and RhLα were corrected online. At least two analyses were performed on each large grain to check for homogeneity.

Single grains of PGMs were selected for laser ablation Re–Os isotope analysis at GEMOC using analytical methods described in detail by Pearson et al. (2002) and Griffin et al. (2002). These analyses were done using a Nu Plasma Multicollector ICP-MS attached to a New Wave/Merchantek UP 213 laser microprobe. Ablation was carried out under the following conditions: frequency of 5 Hz, energies of 1–2 mJ/pulse and a spot size of 30 μm. To monitor any drift in the Faraday cups and ion counters between grains analyzed in different samples a standard NiS bead (PGE-A) with 199 ppm Os (Lorand and Alard, 2001) and ^{187}Os/^{188}Os = 0.1064 (Pearson et al., 2002) was analyzed between the runs. These variations typically were less than 0.1% over a long day analytical session. The overlap of ^{187}Re on ^{187}Os was corrected by measuring the ^{185}Re peak and using ^{187}Re/^{185}Re = 1.6742. All the analyzed grains have ^{187}Re/^{188}Os lower than 0.005, thus ensuring that the isobaric interference of ^{187}Re on ^{187}Os was precisely corrected (cf. Nowell et al., 2008). The data were collected using the Nu Plasma time-resolved software, which allows the selection of the most stable intervals of the signal for integration. The selected interval was divided into 40 replicates to provide a measure of the standard error. Under the ablation conditions described above, for the analyzed grains, having average sizes of >100 μm and average contents of Os > 45 wt.%, a typical run duration of ~75 s was achieved with an average signal intensity of Os ~5 V on the Faraday cups. This gives a precision for ^{187}Os/^{188}Os ranging from 1E−5 to 5.3E−5 (2SE). The accuracy of the data presented here is illustrated by independent analyses (different instruments, operating protocols) of Os–Ir alloys from chromitites in the Luobusa (Tibet) ophiolite. Shi et al. (2007) reported a mean ^{187}Os/^{188}Os = 0.12646 ± 11 (1SE, n = 148) while Pearson et al. (2007) later reported ^{187}Os/^{188}Os = 0.12653 ± 7 (1SE, n = 80). γOs and model ages have been calculated relative to the Os-isotope evolution of enstatite chondrite (present day ^{187}Os/^{188}Os = 0.1281, ^{187}Re/^{188}Os = 0.421, Walker et al., 2002). The quoted uncertainties on T_{MA} and T_{RD} model ages include the uncertainties in the measured ^{187}Os/^{188}Os and ^{187}Re/^{188}Os, calculated according to the equation of Sambridge and Lambert (1997).

4. Results

4.1. PGM characterization

Following the nomenclature of Os–Ir–Ru alloys (Harris and Cabri, 1991), we use the terms "osmium" for Os-rich grains, "iridium" for Ir-rich grains and "ruthenium" for Ru-rich grains. The Os–Ir–Ru solid solutions (or alloys) are represented by osmium, ruthenium, and iridium. The size of the PGMs is usually in the range of 150–500 μm, exceptionally up to 1 mm (the studied grains are from 230 to 800 μm in size). The PGMs are either flat or isometric grains, locally with preserved hexagonal and/or cubic morphology. Some of the grains show deep, hook-shaped fractures (e.g., Fig. 2C), others show a dense leaf-like fracture pattern.

Detailed study of the grains showed that about half are not homogeneous in chemical composition (Fig. 2). They are made up of sharply

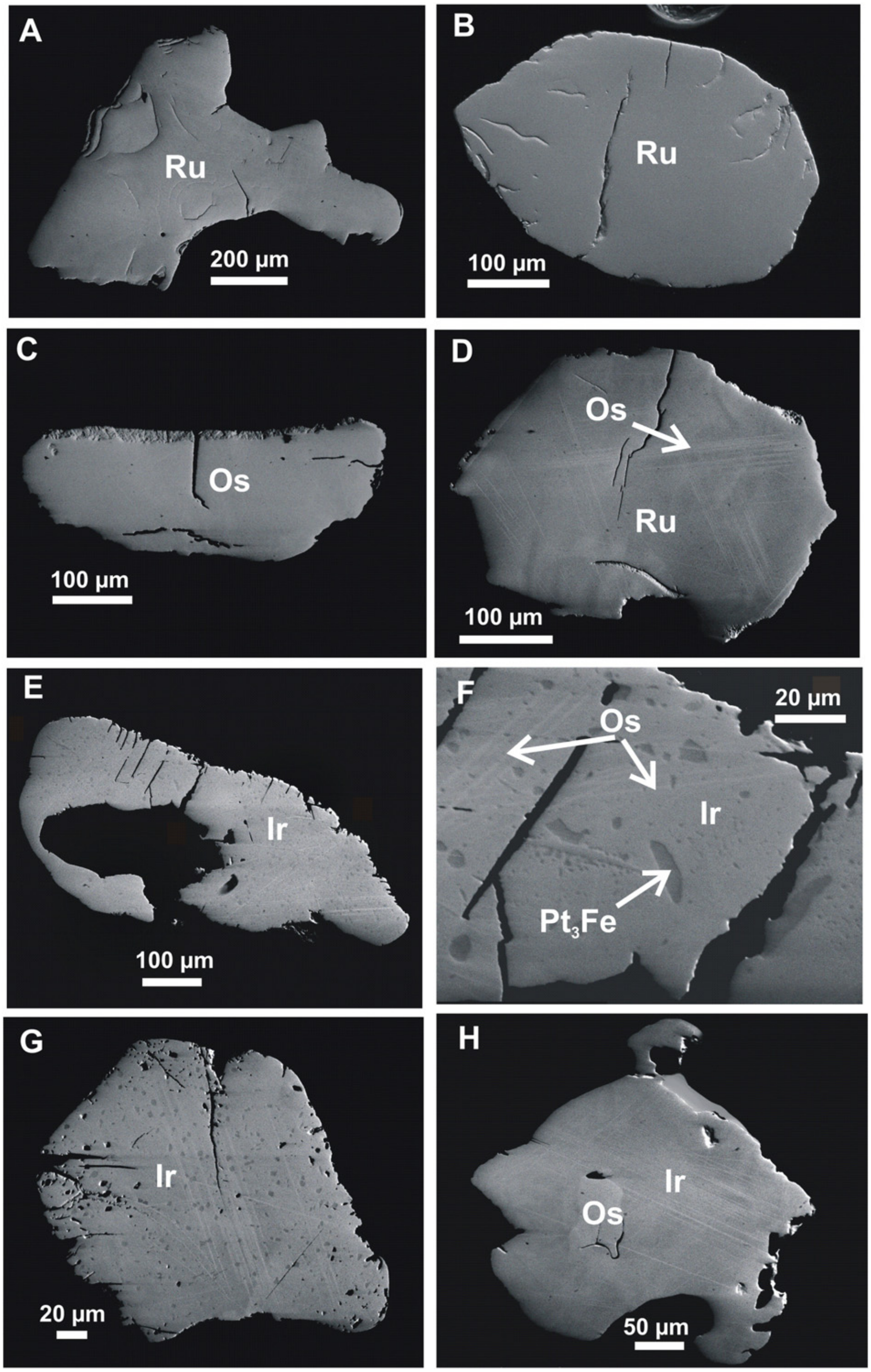

Fig. 2. Mineralogy of PGMs at Vestřev. (A) Back-scattered electron (BSE) image of a monophase ruthenium (grain no. 1, Table 1). (B) BSE image of a monophase ruthenium (grain no. 4, Table 1). (C) BSE image of monophase osmium (grain no. 5, Table 1) with hook-shaped fracture. (D) BSE image of a ruthenium (grain no. 3) intergrown with osmium (Os) and with Os exsolution lamellae. (E) BSE image of an iridium (grain no. 2, Table 1) with microinclusions of Pt–Fe alloy and hongshiite (PtCu), and exsolution lamellae of osmium (Os). (F) BSE image of a detail of Pt–Fe microinclusions and osmium lamellae in iridium (grain no. 2). (G) BSE image of iridium (grain no. 7, Table 1) with microinclusions of Pt–Fe alloy and hongshiite (PtCu), and osmium exsolution lamellae. (H) BSE image of an iridium (grain no. 6, Table 1) with an inclusion of osmium. All photos by J. Malec.

separated phases (either oriented lamellae or elongated inclusions), which differ in Ir, Os, Ru and Fe contents. Some of the grains contain abundant microinclusions of Pt–Fe alloy and rarely hongshiite.

Two ruthenium grains (nos. 1 and 4, Table 1) and one osmium grain (no. 5, Table 1) are very homogeneous without any inclusions or intergrowths (Fig. 2A, B, C). The rest of the analyzed PGM grains are heterogeneous. One ruthenium grain (no. 3) shows intergrowth with osmium and typical osmium exsolution lamellae (Fig. 2D). Iridium grains (nos. 2 and 7) contain inclusions of Pt–Fe–(Ir, Rh), Pt–Cu and texturally youngest exsolution lamellae of osmium (Fig. 2E, F, G). An iridium grain (no. 6) contains inclusions and exsolution lamellae of osmium (Fig. 2H).

Os–Ir–Ru phases (Fig. 3), always have low Fe contents (Table 1). The results of the electron microprobe study are summarized in Tables 1 and 2 and Fig. 3.

Individual osmium grains are compositionally similar to the Os inclusions in ruthenium grains (Table 1). Lower Os (46.4 at.%) and significantly higher Ru (14.9 at.%) concentrations (Table 1) in osmium intergrowths with ruthenium grains (a very narrow up to 10 μm marginal zone — see grain no. 3, Table 1) can be explained in terms of “contamination” by surrounding ruthenium. Individual ruthenium grains show a rather wide range of Ru (32.4–47.2 at.%), Ir (23.6–29.5 at.%) and Os (27.8–36.8 at.%) contents at relatively low Fe (0.4–1.5 at.%; Table 1). The iridium matrix measured on two grains shows a narrow range of Os (34.6–36.8 at.%), Ir (56.6–60.0 at.%), Ru (3.7–4.5 at.%) and Fe (1.7–2.1 at.%) contents. Inclusions and lamellae of iridium in osmium grains show lower contents of Os (21.1–29.0 at.%) and Ru (1.2–1.4 at.%) and higher Ir (66.5–72.6 at.%) and Fe (3.4–5.0 at.%) values than iridium grains. No sulfur was detected in our phases.

4.2. In situ Re–Os isotopic data

The measured Re–Os isotopic compositions of PGMs are listed in Table 3 and plotted in Fig. 4. The values of $^{187}Os/^{188}Os$ ratios of the analyzed phases in the studied Os–Ir–Ru minerals vary between 0.12082 ± 0.00001 and 0.12505 ± 0.00004 (Table 3). $^{187}Re/^{188}Os$ ratios are very low (i.e. <0.00420).

The $^{187}Os/^{188}Os$ in the ruthenium grains ranges from 0.12082 to 0.12505 with an average of 0.12265 ± 0.00003 (2SE, n = 11). $^{187}Re/^{188}Os$ defines a range that extends from 0.00149 ± 0.00002 up to 0.00420 ± 0.00005.

Iridium grains have $^{187}Os/^{188}Os$ ranging from 0.12116 to 0.12351 with an average of 0.12237 ± 0.00002 (2SE, n = 7). $^{187}Re/^{188}Os$ defines a relatively large range that extends from 0.00023 ± 0.00002 up to 0.00199 ± 0.00002.

The $^{187}Os/^{188}Os$ in the osmium grains varies from 0.12280 to 0.12402 with an average of 0.12341 ± 0.00003 (2SE, n = 6). This is within the range of the ruthenium grains. $^{187}Re/^{188}Os$ values are from 0.00017 ± 0.00002 to 0.00150 ± 0.00005.

The lowest subchondritic values of the $^{187}Os/^{188}Os$ ratios (0.12082–0.12111) were detected in a ruthenium grain no. 1 (T_{MA} = 1.0–1.4 Ga, Table 3). The most radiogenic $^{187}Os/^{188}Os$ ratios (0.12494–0.12505) were found in a ruthenium grain no. 4 (T_{MA} = 0.43–0.45 Ga, Table 3).

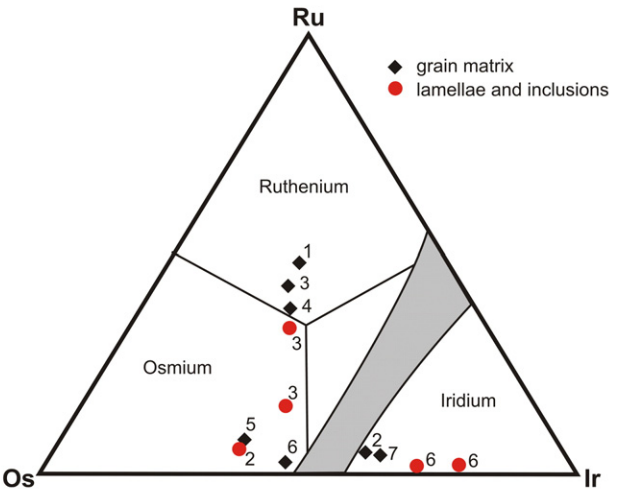

Fig. 3. Chemical composition of platinum-group element alloys from Vestřev (individual fields for ruthenium, osmium, iridium, osmiridium and the miscibility gap between hexagonal and cubic species are from Harris and Cabri (1991)).

The consistency between T_{MA} and T_{RD} model ages (Table 3) reflects the low Re/Os of all grains. The model-age data are summarized in Fig. 5. Clearly, there is no observable isotopic difference between monophase and polyphase grains. The T_{MA} of the two monophase ruthenium grains (nos. 1 and 4) cover a wide range, from 0.43 to 1.04 Ga; a monophase osmium (grain 5) has a model age of 0.58–0.59 Ga. The remaining polyphase ruthenium, iridium and osmium grains (nos. 2, 3, 6 and 7) show model ages from 0.63 to 0.98 Ga.

5. Discussion

5.1. Primary sources of PGM and garnet

In many cases, PGMs in placers can be traced to the source rocks (e.g., ophiolites, or the zoned ultramafic intrusions known as Uralian-Alaskan-type complexes; Foley et al., 1997; Garuti et al., 1997; Cabri et al., 1996 and references therein). At Vestřev, it is difficult to identify the primary sources of Os, Ir, Ru and Pt minerals because there are no indications of PGE mineralization reported either from the drainage area of the Kalenský brook or from the whole area of the Krkonoše Piedmont Basin. Black shales which occur in the Kalenský horizon (Permian) have not been analyzed for PGEs so far, but black shales of similar age from the Rudnice horizon which do not crop out in the drainage area of the Kalenský brook yield Pt, Pd and Rh values mostly between 1 and 5 ppb, max. 7 ppb (Pašava, 1991), which are comparable with mantle values. It is apparent that the PGM assemblage found at Vestřev placer

Table 1
Elemental composition of Os–Ir–Ru minerals from Vestřev.

Grain no.	Mineral	Os	Ir	Ru	Fe	Sum wt.%	Os	Ir	Ru	Fe	Sum atom.%	apfu Os	Ir	Ru	Fe
1	Ruthenium (matrix)	36.01	30.84	32.45	0.57	99.87	27.80	23.56	47.15	1.49	100	0.28	0.24	0.47	0.01
2	Iridium (matrix with Pt–Fe–(Ir.Rh) inclusions)	37.13	57.83	2.40	0.63	97.99	36.76	56.64	4.46	2.14	100	0.37	0.57	0.04	0.02
2	Osmium (lamellae and a long bent inclusion)	61.82	35.06	2.80	0.33	100.01	60.08	33.71	5.12	1.09	100	0.60	0.34	0.05	0.01
3	Ruthenium (matrix)	39.48	30.76	27.20	0.29	97.73	32.35	24.94	41.92	0.80	100	0.32	0.25	0.42	0.01
3	Osmium (islet at the margin)	43.61	35.32	20.41	0.42	99.76	36.84	29.52	32.43	1.21	100	0.37	0.30	0.32	0.01
3	Osmium (narrow marginal zone in corner)	49.79	38.58	8.53	0.99	97.89	46.37	35.55	14.94	3.14	100	0.46	0.36	0.15	0.03
4	Ruthenium (matrix)	40.55	33.70	23.08	0.15	97.49	34.42	28.31	36.86	0.42	100	0.34	0.28	0.37	0.00
5	Osmium (matrix)	59.38	35.57	3.91	0.10	98.96	58.06	34.42	7.19	0.33	100	0.58	0.34	0.07	0.00
6	Osmium (matrix)	54.49	43.54	1.27	0.93	100.22	52.84	41.78	2.32	3.06	100	0.53	0.42	0.02	0.03
6	Iridium (large inclusion)	29.23	67.82	0.63	1.00	98.68	28.96	66.49	1.17	3.38	100	0.29	0.66	0.01	0.03
6	Iridium (thin lamella)	21.06	73.31	0.72	1.46	96.55	21.08	72.61	1.35	4.96	100	0.21	0.73	0.01	0.05
7	Iridium (matrix with inclusions of Pt–Fe–(Ir.Rh) and Pt–Cu and a lamellae of osmium)	34.06	59.67	1.92	0.50	96.14	34.61	59.99	3.66	1.74	100	0.35	0.60	0.04	0.02

Table 2
Elemental composition of inclusions from Vestřev.

Grain no.	Pt	Fe	Ir	Rh	Cu	sum wt.%	Pt	Fe	Ir	Rh	Cu	sum atom.%	apfu Pt	Fe	Ir	Rh
2	84.9	8.9	4.9	0.6	n.d.	99.3	69.67	25.40	4.09	0.85	n.d.	100	2.79	1.02	0.16	0.03
7	82.7	9.5	6.7	0.7	n.d.	99.6	66.70	26.78	5.52	1.01	n.d.	100	2.67	1.07	0.22	0.04
													apfu Pt	Cu		
7	72.6				23.6	96.2	50.08				49.92	100	1.00	1.00		

(dominant Pt–Fe alloys accompanied by Os–Ir–Ru alloys without other Pt- or Pd-minerals) is very different from those in Rožany, Kunratice (Pt–Pd–As, Pašava et al., 2001) and Staré Ransko (Pt–As and Pd–Bi–Te, Pašava et al., 2003; Ackerman et al., 2013a), both of which are ca 100 km from Vestřev (Fig. 1). However, similar PGM associations were reported from the Danubian fluvial Au-PGE placers in the Bayerischer Wald in NE Bavaria (Germany) where native Au, Au–Hg, Au–Ag–Cu alloys (argentocuproaurite), Ir–Rh–As sulfide, PtAs, Pt–Fe, Ir–Os and Ru–Ir–Os alloys were found (Dill et al., 2009). Based on mineral assemblages and morphological studies, these authors suggested that the PGMs were derived from meta-(ultra)basic igneous rocks (ophiolites) bounded by shear-zones with strong hydrothermal alteration, which are found squeezed into the paragneisses of the Moldanubian Zone. Other PGM assemblages similar to what we have found at Vestřev have been reported from ophiolite-hosted chromitites and related placers from different parts of the world (e.g., Economu-Eliopoulos, 1996; Tolstykh et al., 2002b, 2009; González-Jiménez et al., 2009 and references cited therein) and from placers associated with Uralian-Alaskan type intrusions (e.g., Nizhni Tagil-Siberian Platform, Russia — Malitch and Thalhammer, 2002; Johan, 2006; British Columbia, Canada — Barkov et al., 2005; Russian Far East — Shcheka et al., 2004; Koryak-Kamchatka Platinum Belt, Russia — Tolstykh et al., 2002c).

The compositions of the Os–Ir–Ru minerals from Vestřev show a vertical trend from Os to Ru for the hexagonal phases (Fig. 3), consistent with the experimental work of Bird and Bassett (1980) on Os–Ir–Ru alloys. According to Krivenko and Tolstykh (1994), Tolstykh et al. (2002b) and Weiser (2004), this points to a primary origin related to an ophiolitic complex.

The association of heavy minerals identified in the Vestřev placer deposit does not necessarily aid identification of a PGE source in the drainage area of the Permian sediments. Hematite, which predominates in the heavy concentrate, is most likely a product of diagenesis of Permian sandstones. It looks completely different from itabirites (a laminated, metamorphosed oxide-facies iron formation), which can host PGE mineralization (e.g. Au–Pd–Pt mineralization reported by Kwitko et al. (2002) from Jacutinga, in the Itabira district of Brazil).

The morphology of pyrope-rich garnet grains from Vestřev (mostly rounded and corroded, but also with numerous euhedral/subhedral grains; Bauer and Hříchová, 1966), indicates a possible combination of several factors, including different distances of transportation and intensive corrosion by humic acids (Martínek and Štolfová, 2009). Some of the PGM grains at Vestřev show disintegration and/or corrosion while some of them have locally preserved hexagonal and/or cubic morphology. It has been documented by many authors that primary PGE-

Table 3
Re–Os composition of Os–Ir–Ru minerals from Vestřev.

Sample/grain	μm	Mineral	$^{187}Os/^{188}Os$	2 SE	$^{187}Re/^{188}Os$	2 SE	γ Os^{ECR}	T_{Ma}^{ECR} (Ga)	T_{RD}^{ECR} (Ga)	2 SE (Ga)[a]
Vestřev 1–4	800	Ruthenium	0.12110	0.00004	0.00349	0.00004	−5.47	1.00	0.99	0.01
Vestřev 1–5		Ruthenium	0.12105	0.00002	0.00367	0.00003	−5.51	1.01	1.00	0.00
Vestřev 1–6		Ruthenium	0.12097	0.00001	0.00385	0.00005	−5.56	1.02	1.01	0.00
Vestřev 1–7		Ruthenium	0.12091	0.00004	0.00359	0.00003	−5.61	1.03	1.02	0.01
Vestřev 1–8		Ruthenium	0.12082	0.00003	0.00364	0.00003	−5.68	1.04	1.03	0.00
Vestřev 3–1	400	Ruthenium	0.12357	0.00004	0.00402	0.00003	−3.54	0.65	0.64	0.01
Vestřev 3–1		Ruthenium	0.12345	0.00003	0.00403	0.00004	−3.63	0.67	0.66	0.00
Vestřev 3–2		Ruthenium	0.12354	0.00003	0.00407	0.00003	−3.56	0.65	0.65	0.00
Vestřev 3–4		Ruthenium	0.12372	0.00003	0.00420	0.00004	−3.42	0.63	0.62	0.00
Vestřev 4–2	490	Ruthenium	0.12505	0.00003	0.00149	0.00003	−2.38	0.43	0.43	0.00
Vestřev 4–3		Ruthenium	0.12494	0.00001	0.00152	0.00002	−2.47	0.45	0.45	0.00
		Min	0.12082	0.00001	0.00149	0.00002	−5.68	0.43	0.43	0.00
		Max	0.12505	0.00004	0.00420	0.00005	−2.38	1.04	1.03	0.01
		Avg	0.12265	0.00003	0.00342	0.00003	−4.26	0.78	0.77	0.00
Vestřev 2–1	700	Iridium	0.12116	0.00002	0.00028	0.00002	−5.42	0.98	0.98	0.00
Vestřev 2–2		Iridium	0.12119	0.00002	0.00028	0.00002	−5.39	0.98	0.98	0.00
Vestřev 2–3		Iridium	0.12239	0.00002	0.00023	0.00002	−4.45	0.81	0.81	0.00
Vestřev 2–4		Iridium	0.12240	0.00003	0.00030	0.00002	−4.45	0.81	0.81	0.00
Vestřev 2–5		Iridium	0.12244	0.00002	0.00031	0.00002	−4.42	0.80	0.80	0.00
Vestřev 7–1	230	Iridium	0.12349	0.00003	0.00195	0.00002	−3.60	0.66	0.65	0.00
Vestřev 7–2		Iridium	0.12351	0.00002	0.00199	0.00002	−3.59	0.65	0.65	0.00
		Min	0.12116	0.00002	0.00023	0.00002	−5.42	0.65	0.65	
		Max	0.12351	0.00003	0.00199	0.00002	−3.59	0.98	0.98	
		Avg	0.12237	0.00002	0.00076	0.00002	−4.47	0.81	0.81	
Vestřev 5–1	460	Osmium	0.12402	0.00002	0.00148	0.00002	−3.19	0.58	0.58	0.00
Vestřev 5–2		Osmium	0.12397	0.00002	0.00150	0.00002	−3.22	0.59	0.59	0.00
Vestřev 5–3		Osmium	0.12396	0.00002	0.00149	0.00002	−3.23	0.59	0.59	0.00
Vestřev 6–1	270	Osmium	0.12285	0.00003	0.00075	0.00003	−4.10	0.75	0.74	0.00
Vestřev 6–2		Osmium	0.12280	0.00003	0.00066	0.00003	−4.14	0.75	0.75	0.00
Vestřev 6–3		Osmium	0.12284	0.00005	0.00017	0.00005	−4.10	0.75	0.74	0.01
		Min	0.12280	0.00002	0.00017	0.00002	−4.14	0.58	0.58	0.00
		Max	0.12402	0.00005	0.00150	0.00005	−3.19	0.75	0.75	0.01
		Avg	0.12341	0.00003	0.00101	0.00003	−3.66	0.67	0.67	0.00

γOs and model ages calculated by comparison with enstatite chondrite ($^{187}Os/^{188}Os = 0.1281$; $^{187}Re/^{188}Os = 0.421$; Walker et al., 2002).

[a] Propagated 2SE analytical uncertainties on $^{187}Os/^{188}Os$ and $^{187}Re/^{188}Os$.

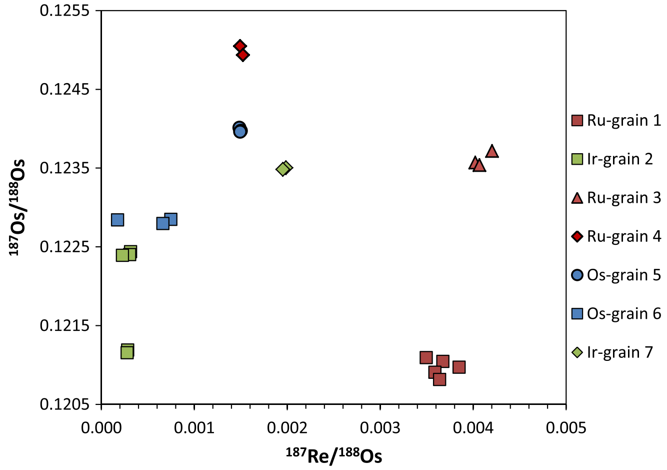

Fig. 4. $^{187}Re/^{188}Os$ *vs* $^{187}Os/^{188}Os$ plot for PGMs from Vestřev.

ophiolite-type rocks can contain PGM grains of different morphologies (from euhedral via subhedral to anhedral, e.g., Oberthür et al., 2003; Uysal et al., 2005; Prichard et al., 1986; Zaccarini et al., 2008 and references cited therein). For example, Prichard et al. (2014) showed that PGMs weathered from chromitites in the Shetland ophiolite complex and transported for a short distance (up to 50 m from the PGE-rich rocks) preserve their composition and often euhedral shapes, but with increased distance they show signs of disintegration.

Seifert and Vrána (2005) suggested that pyrope-rich garnet at Vestřev could have a source in the České středohoří Mountains or Sowie Gory, where ultrabasic garnet-bearing peridotites occur; Martínek and Štolfová (2009) proposed garnet peridotite of uncertain location as a source of the pyrope at Vestřev. We have no evidence that garnet and PGMs at Vestřev were derived from similar sources, but it should be noted that occurrences of PGMs in abyssal and orogenic peridotites have been reported recently. For example, Luguet et al. (2003, 2007) and Lorand et al. (2010) described Ru–Os–Ir sulfides (laurite–erlichmanite), Pt–Ir–Os alloys and Pt–Pd–Te–Bi phases from peridotites on the Mid-Atlantic Ridge and in the Pyrenees. In the Bohemian Massif, Ackerman et al. (2013b) found Pt–As (sperylite) and an unidentified Os–Ru phase in peridotites from the Horní Bory (Gföhl Unit, Moldanubian Zone). Further, laurite (RuS_2) has been discovered in a chromite-rich layer in the Mohelno peridotite body (SE Moravia; Ackerman — unpub. data). Thus we cannot exclude peridotite as a possible host rock for the PGM found at Vestřev.

5.2. $^{187}Os/^{188}Os$ variability in the PGM

Osmium isotopes are an important tracer of the evolution of highly siderophile elements in the upper mantle. The depleted upper mantle, as sampled by abyssal peridotites and the mantle sections of ophiolites, constitutes one of the most important geochemical reservoirs, which is not yet well constrained in a way of melt extraction as well as recycling of crustal material. Primary Os-rich PGMs (e.g., laurite (RuS_2)–erlichmanite (OsS_2) series and Os–Ir–Ru alloys), which form inclusions in chromites, are particularly well protected by the host mineral and are thus likely to retain the Os isotopic values of their source, at the time they crystallized. This makes chromites and associated alloy phases ideal material to investigate the Os isotopic composition and evolution of the convective upper mantle and/or to quantify the geochemical heterogeneity of this reservoir through time (Walker et al., 2002; Meibom et al., 2002; Pearson et al., 2007; González-Jiménez et al., 2014 and references cited therein).

A wide range of subchondritic $^{187}Os/^{188}Os$ values has been found in 'primary' PGM assemblages (e.g., laurite and Os-rich alloys) from ophiolite-type complexes worldwide (e.g., Malitch et al., 2002; Malitch, 2004; Ahmed et al., 2006; Shi et al., 2007; González-Jiménez et al., 2014 and references cited therein). The average value of $^{187}Os/^{188}Os = 0.12276$ ($n = 24$) in our PGM is in the range of Ru–Os sulfides from podiform chromitites in the ophiolite mantle section at Kraubat, Austria (0.11249–0.12437; Malitch, 2004), base metal and PGE sulfides from ophiolitic podiform chromitite at Caridad, Cuba (0.1203–0.1274; González-Jiménez et al., 2012), PGM from the Mayari-Cristal ophiolite massif in eastern Cuba (0.1185–0.1274;

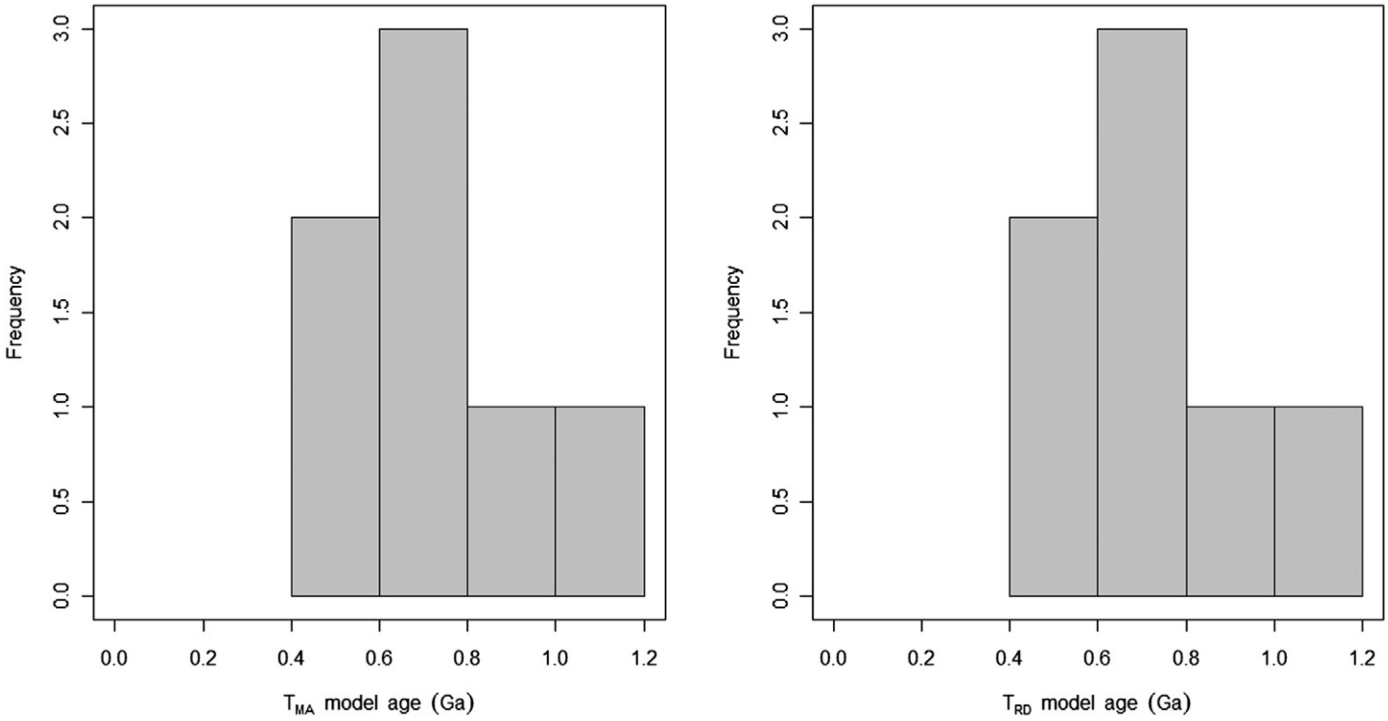

Fig. 5. Frequency distribution histogram of Os model ages (T_{MA} and T_{RD}, Ga) for PGMs at Vestřev (R language; www.r-projekt.org).

Marchesi et al., 2011), PGM from the central Eastern Desert ophiolite-hosted chromitites in Egypt (0.1226 on average; Ahmed et al., 2006), PGM from placer deposits in clinopyroxenite/dunite massifs of the Siberian Platform in Russia (0.1185 to 0.1274; Malitch et al., 2002), and PGM from ophiolite-related deposits of the Urals and Timan (0.1134 to 0.1262; Kostoyanov, 1988). This wide range is consistent with a model in which a prolonged history of melting events has affected the parent ultramafic source rocks in the mantle. This variability is in agreement with the conclusion that the Os-isotope system of PGM records multiple events during the chemical differentiation history of the mantle (Carlson, 2002). If we compare our γOs data with previously published ophiolitic datasets world-wide that include a significant number of analyzed PGM grains (Shi et al., 2007), we see that they fall into a group with significant scattering toward unradiogenic values (i.e., $\gamma Os < -1$ as in the Josephine ophiolite, Meibom et al., 2002, 2004; Walker et al., 2005; and the Dongqiao II peridotite, Shi et al., 2007).

Crustal rocks throughout the Bohemian Massif are dominated by Variscan (~0.38 to ~0.28 Ga) and Cadomian (0.50 to 0.55 Ga) lithologies (Vrána and Štědrá, 1997; Cháb et al., 2010). On the other hand, Nd $_{TDM}$ model ages for the majority of the Variscan crustal rocks range between 1.25 and 1.85 Ga (e.g., Gebauer et al., 1989; Janoušek et al., 1995). The whole age range for our samples (0.43–1.03 Ga) is roughly similar to T_{RD} model ages (between 0.5 and 1.3 Ga) reported for the mantle peridotites from the Bohemian Massif (between 0.5 and 1.3 Ga — see Ackerman et al., 2009; Medaris et al., 2009; Ackerman et al., 2013a, 2013b and others). This implies that partial melting was a pre-Variscan event. Furthermore, our range is consistent with T_{RD} model ages obtained from the study of the European–Mediterranean lithosphere (González-Jiménez et al., 2013), which were linked to crustal growth events, mainly during supercontinent assembly and/or breakup at ca. 1.8, 1.1., 0.9, 0.6 and 0.3 Ga. Therefore we suggest that the distribution of Os model ages from Vestřev PGM provides evidence for the long history of melt depletion that affected the mantle sources of PGM in the Bohemian Massif.

6. Conclusions

Very rare grains of Pt–Fe alloy accompanied by osmium, Ir and Ru alloys, locally with inclusions of Pt–Fe alloy and hongshiite (PtCu), have been identified in the heavy fraction of the Quaternary pyrope-rich garnet placer at Vestřev (Krkonoše Piedmont Basin, Bohemian Massif). Besides rare inclusions in ruthenium and osmium grains, the remaining PGMs are heterogeneous. This mineralogical association is typical for various ophiolite-type settings; this is consistent with the chemistry of our Os–Ir–Ru minerals, which show a typical Ru-trend. The morphology and type of corrosion of garnet and PGM grains does not exclude that they were weathered and transported from similar source rocks.

In-situ analyses of the Os-rich phases show heterogeneous Os-isotope compositions ($^{187}Os/^{188}Os = 0.12082–0.12505$, average $= 0.12276$) and negative γOs, indicating a subchondritic mantle source of PGEs, which is consistent with a close association between the PGM from Vestřev and mantle-derived rocks. The Os model ages from ~0.4 to ~1.0 Ga are similar to T_{RD} model ages (between 0.5 and 1.3 Ga) reported for mantle peridotites from the Bohemian Massif and most likely reflect long history of melt depletion that affected the mantle sources of the PGM.

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