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LAURITE AND RUARSITE FROM PODIFORM CHROMITITES AT KRAUBATH AND HOCHGRÖSSEN, AUSTRIA: NEW INSIGHTS FROM OSMIUM ISOTOPES

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Abstract

The chemical and osmium-isotope composition of platinum-group minerals (PGM) [*e.g.*, laurite–erlichmanite (RuS_2–OsS_2), ruarsite–osarsite (RuAsS–OsAsS) series and Os–Ir alloy (Os,Ir)] from variably altered podiform chromitites of the Kraubath and Hochgrössen dunite–harzburgite massifs are reported for the first time. These massifs, the largest dismembered mantle relics in the Eastern Alps of Austria, were interpreted as a strongly metamorphosed ophiolite sequence, which forms part of the Speik Complex. Unaltered podiform chromitites from both localities display negatively sloped chondrite-normalized platinum-group element (PGE) patterns. The highly altered podiform chromitite at Kraubath is dominated by less refractory PGE (PPGE: Pd, Pt, Rh) over refractory PGE (IPGE: Os, Ir and Ru). The chemical composition of chromite varies from a Cr# [100*Cr/(Cr + Al)] of 74 to 87 and a Mg# [100*Mg/(Mg + Fe^{2+})] of 44 to 61, values typical of podiform chromitites from the mantle section of an ophiolite. The PGM assemblage in the unaltered podiform ores is dominated by laurite (43% and 75% of all PGM at Kraubath and Hochgrössen, respectively). Sperrylite, $PtAs_2$, is the most abundant PGM (61%) in the altered chromitite, whereas minerals of laurite–erlichnmanite series are subordinate (4%). At Kraubath, Os-bearing PGM (laurite, erlichmanite, ruarsite and Os–Ir alloy) occur as (a) single grains and (b) complex polyphase assemblages. At Hochgrössen, laurite and Os–Ir alloy are present as solitary grains only. *In situ* osmium-isotope measurements of 16 PGM grains from bedrock (*e.g.*, laurite and ruarsite) by laser-ablation multiple-collector inductively coupled plasma – mass spectrometry (LA–MC–ICP–MS) revealed low $^{187}Os/^{188}Os$ and $\gamma Os_{t=0}$ values, indicative of a subchondritic source of the PGE in the mantle. Combined with less radiogenic Os isotopic values measured by negative thermal ionization mass spectrometry (N–TIMS), $^{187}Os/^{188}Os$ ranges from 0.11580 to 0.12437, and $\gamma Os_{t=0}$ values,

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from –9.97 to –3.31, respectively. The Os isotopic composition of PGM from altered chromitite at Kraubath is similar or even less radiogenic than that from typical podiform chromitite. The Re–Os system within PGM thus has not been disturbed during later metamorphic events. Furthermore, the wide range of $^{187}Os/^{188}Os$ values is similar to that in detrital Os-rich alloys derived from other dunite–harzburgite complexes worldwide (*i.e.*, $\gamma Os_{t=0}$ ranges from –14.95 to –2.12). On the basis of the osmium isotopic composition of laurite and ruarsite, ultramafic protoliths in the Speik ophiolite complex yield model ages in the range of 1758 to 584 Ma. The mineral-isotopic data are consistent with a prolonged melting history of the parent ultramafic rocks from the mantle section of an ophiolite and provide further evidence for the closed-system behavior of the Re–Os isotopic system within PGM.

Keywords: laurite, ruarsite, LA–MC–ICP–MS study, osmium isotopes, chromitite, ophiolite, upper mantle, Kraubath, Hochgrössen, Austria.

Sommaire

Nous avons déterminé pour la première fois la composition chimique et les rapports isotopiques d'osmium des minéraux du groupe du platine [*e.g.*, des séries laurite–erlichmanite (RuS_2–OsS_2) et ruarsite–osarsite (RuAsS–OsAsS) et de l'alliage Os–Ir (Os,Ir)] provenant de chromitites podiformes variablement altérées des massifs à dunite–harzburgite de Kraubath et Hochgrössen. Ces massifs, les plus volumineux représentants du manteau démembré des Alpes orientales en Autriche, étaient attribués à une séquence ophiolitique fortement métamorphisée faisant partie du complexe de Speik. Les chromitites podiformes non altérées des deux endroits montrent une courbe à pente négative dans un diagramme illustrant les teneurs en éléments du groupe du platine (normalisées par rapport aux concentrations chondritiques). Les échantillons de chromitite fortement altérés à Kraubath montrent une dominance des éléments moins réfractaires (Pd, Pt, Rh) par rapport aux éléments réfractaires (Os, Ir, Ru). La composition du spinelle chromifère varie en Cr# [100*Cr/(Cr + Al)] de 74 à 87 et en Mg# [100*Mg/(Mg + Fe^{2+})] de 44 à 61, valeurs typiques pour les chromitites podiformes de la section mantellique d'une ophiolite. Le minerai podiforme non altéré contient surtout la laurite (43% et 75% de tous les grains de minéraux du groupe du platine à Kraubath et Hochgrössen, respectivement). La sperrylite, $PtAs_2$, est davantage abondante (61%) dans la chromitite altérée, tandis que les membres de la série laurite–erlichmanite sont subordonnés (4%). A Kraubath, les minéraux porteurs d'osmium (laurite, erlichmanite, ruarsite at alliage Os–Ir) se présentent (a) en grains individuels et (b) en assemblages complexes polyphasés. A Hochgrössen, la laurite et l'alliage Os–Ir sont présents en grains isolés seulement. Nos analyses isotopiques *in situ* de seize grains de ces minéraux (*e.g.*, laurite et ruarsite) par analyse sur plasma avec couplage inductif, spectrométrie de masse, ablation au laser et avec multicollecteurs révèle de faibles valeurs du rapport $^{187}Os/^{188}Os$ et de $\gamma Os_{t=0}$, indications d'une source subchondritique des éléments du groupe du platine dans le manteau. Considérés à la lumière des valeurs isotopiques moins radiogéniques obtenues par spectrométrie de masse par ionisation thermique négative (N–TIMS), $^{187}Os/^{188}Os$ varie de 0.11580 à 0.12437, et $\gamma Os_{t=0}$ varie de –9.97 à –3.31, respectivement. La composition isotopique de l'osmium des minéraux du groupe du platine provenant de la chromitite altérée à Kraubath est semblable, voire même moins radiogénique, que ce qui est typique d'une chromitite podiforme typique. Le système Re–Os n'a donc pas subi de modification au cours des événements ultérieurs. De plus, l'intervalle étendu de valeurs de $^{187}Os/^{188}Os$ ressemble à celle d'alliages riches en osmium d'origine détritique, dérivés d'autres complexes à dunite–harzburgite à l'échelle mondiale (*i.e.*, $\gamma Os_{t=0}$ dans l'intervalle de –14.95 à –2.12). Selon la composition isotopique de l'osmium dans la laurite et la ruarsite, les protolithes ultramafiques du complexe ophiolitique de Speik ont un âge modèle dans l'intervalle de 1758 à 584 Ma. Les données isotopiques déterminées étayent l'hypothèse d'un épisode prolongé de fusion partielle d'un socle ultramafique dans la section mantellique de l'ophiolite et du comportement en système isotopique fermé de Re–Os dans ces minéraux.

(Traduit par la Rédaction)

Mots-clés: laurite, ruarsite, étude ICP–MS avec ablation au laser et multicollrcteurs, isotopes d'osmium, chromitite, ophiolite, manteau supérieur, Kraubath, Hochgrössen, Autriche.

Introduction

Recent Os-isotope studies have clearly shown that the Os isotopic system of minerals like chromite, olivine, base-metal (BM) sulfides, and Os-rich alloy, may contribute to a better understanding and more accurate interpretation of the processes leading to fractionation of Os isotopes in different environments in the mantle (Burton *et al*. 1999, 2000, Standish *et al*. 2001, Alard *et al*. 2002, Malitch *et al*. 2002a, Meibom & Frey 2002, Pearson *et al*. 2002, Spetsius *et al*. 2002, among others). Taking into consideration that Ru–Os sulfides encapsulated in chromian spinel retain primordial Os-isotope signatures, these platinum-group minerals (PGM) are very promising targets to avoid ambiguity in the interpretation of whole-rock Os isotopic results.

To our knowledge, few Os isotopic analyses of bedrock Ru–Os sulfides have been done from an ophiolitic environment. Results of three analyses of laurite measured with the MIT–Harvard–Brown Cameca 3f ion microprobe have been reported by Hattori *et al.* (1992). Two other sets of Os isotopic results on laurite have been presented, by Walker *et al.* (1996) and Ohnenstetter *et al.* (1999). To fill this gap and to demonstrate the high potential of Os isotopes measured in bedrock PGM, we conducted a detailed laser-ablation (LA) multiple collector – inductively coupled plasma – mass spectrometry (MC–ICP–MS) study of single and polyphase

Os-rich PGM grains, which comprise laurite, $(Ru,Os)S_2$, and ruarsite, (Ru,Os)AsS. These PGM were liberated from variably altered podiform chromitites of the Kraubath (Malitch *et al.* 2001b) and Hochgrössen (this study) dunite–harzburgite massifs, the largest dismembered mantle relics in the Eastern Alps, Austria (Fig. 1).

Our aim in this paper is to discuss for the first time results of LA–MC–ICP–MS isotopic analyses of Ru–Os sulfides and sulfarsenides from variably altered podiform chromitites at Kraubath and Hochgrössen in order to: (1) test the closed-system behavior of the Re–Os isotopic system within PGM, (2) determine the

FIG. 1. Tectonic scheme of the Eastern Alps (a) and schematic geological map of Middle Austroalpine units east of the Tauern Window, showing the location of the Hochgrössen, Kraubath and Pernegg ultramafic massifs (b), after Frank (1987) and Neubauer (1988), respectively.

source of the PGE (*e.g.*, chondritic, subchondritic, suprachondritic mantle), (3) establish if the PGM from podiform chromitites are isotopically similar at all localities, and (4) provide age constraints on the formation of ultramafic protolith hosting the PGE mineralization.

In the past, some Os isotope data have been presented without reporting the mineral chemistry of Os-rich PGM (Hart & Kinloch 1989, Hirata *et al.* 1998, Meibom & Frey 2002, among others). To ultimately characterize the PGM from the podiform chromitites for which LA–MC–ICP–MS analyses have been performed, the composition of Os-bearing PGM (*e.g.*, laurite–erlichmanite and ruarsite–osarsite series) also is presented, along with bulk platinum-group elements (PGE) concentrations in mantle-derived chromitites.

BACKGROUND INFORMATION

Re–Os is potentially the best isotopic system with which to determine mantle-depletion ages for ultramafic rocks. Owing to considerable progress in the development of analytical techniques in recent years, it has been widely applied in evaluating distinct sources and dating melting events in the mantle in different geological settings (Reisberg & Lorand 1995, Snow & Reisberg 1995, Roy-Barman *et al.* 1996, Walker *et al.* 1996, Handler *et al.* 1997, Nägler *et al.* 1997, Hirata *et al.* 1998, Parkinson *et al.* 1998, Shirey & Walker 1998, Burton *et al.* 1999, Blusztajn *et al.* 2000, Bowles *et al.* 2000, Brandon *et al.* 2000, Malitch *et al.* 2000, Alard *et al.* 2002, Malitch 2002, Malitch & Thalhammer 2002, among many others). Recent Os isotopic results for bulk rocks and ultramafic xenoliths led to the conclusion that the Re–Os system may have been disturbed by interaction with melt or fluid (Brandon *et al.* 1996, 1998, Peslier *et al.* 2000, Becker *et al.* 2001), thus questioning the closed-system behavior of the Re–Os system. In addition, ambiguity in interpretation of whole-rock Os isotopic data also arose from mineral Os isotopic studies, which proved Os heterogeneity in mantle minerals even in one sample (Burton *et al.* 1999, 2000, Alard *et al.* 2001a, b, 2002, among others). Alard *et al.* (2001b, 2002) documented two generations of isotopically distinct BM sulfides, which may occur even in one peridotite xenolith. Subordinate BM sulfides enclosed in olivine had unradiogenic Os isotope composition, whereas dominant pyroxene-hosted or interstitial BM sulfide were much more radiogenic (^{187}Os/^{188}Os up to 0.159), contributing in different proportions to the radiogenic whole-rock Os isotope composition. Thus, the primordial signature of BM sulfide enclosed in silicate is masked by highly radiogenic secondary BM sulfide, which cannot be estimated from the whole-rock Os isotope systematics alone. Furthermore, *in situ* LA–MC–ICP–MS analyses of BM sulfides from abyssal and ophiolitic peridotites indicate a wide range of ^{187}Os/^{188}Os values, from 0.1113 ± 0.0008 to 0.1382 ± 0.0014 (Alard *et al.* 2001a), which are in obvious disagreement with the average estimates for both (1) depleted mid-ocean ridge (MOR) mantle (DMM; 0.1246 ± 0.0014) deduced from whole-rock Os isotopic composition of abyssal peridotites (Snow & Reisberg 1995) and (2) primitive upper mantle (PUM; 0.1296 ± 0.0008) defined on the basis of whole-rock Os isotopic data for mantle xenoliths (Meisel *et al.* 2001).

Chromite, as the most resistant mantle mineral, is well protected from high-temperature serpentinization and low-temperature ocean-floor weathering in an ophiolite environment, and, thus, has been proposed to represent initial ^{187}Os/^{188}Os values (Walker *et al.* 2002). However, it has been shown that the Os budget of the mantle is mainly controlled by sulfide and alloy (Martin *et al.* 1993, Hart & Ravizza 1996, Burton *et al.* 1999). Therefore, inclusions of Os-rich platinum-group minerals (PGM) in chromite, commonly the earliest precipitates in ultramafic systems, are the best mineral phases to constrain initial ^{187}Os/^{188}Os values and to avoid ambiguity in the interpretation of Os isotopic results in oceanic mantle.

The advantage of the Re–Os system applied to Os-rich minerals is that PGM contain osmium as a main or trace element in their crystal structures, and are essentially devoid of Re. This feature allows one to obtain accurate initial Os isotope values, assuming that the Os isotopic composition of PGM has not changed after their formation and, thus, reflects that of the source. Furthermore, since osmium is one of the six PGE, Os isotopes are particularly useful (1) to distinguish between crustal and mantle sources for PGE due to the large fractionation of Re over Os between crust and mantle, and (2) to date Ru–Os sulfides and Os–Ru–Ir alloys of mantle origin. Both approaches have been applied in detail to PGM from placer deposits derived mainly from dunite–harzburgite (*e.g.*, of Alpine or ophiolite type) and clinopyroxenite–dunite (*e.g.*, of zoned, Uralian, Alaskan or Aldan type) massifs (Allègre & Luck 1980, Hattori & Hart 1991, Hattori *et al.* 1992, Hattori & Cabri 1992, Borg & Hattori, 1997, Lyon *et al.* 1997, Hirata *et al.* 1998, Malitch & Kostoyanov 1998, 1999, Bird *et al.* 1999, Malitch 1999, Ohnenstetter *et al.* 1999, Rudashevsky *et al.* 1999, Malitch *et al.* 2001c, 2002a, b, Malitch & Badanina 2002, Malitch & Thalhammer 2002, Meibom & Frey 2002). Therefore, Os-rich PGM, in most cases the earliest precipitates in ultramafic systems, are potentially the best tracers of melting events that might be unequivocally recognized during the formation of the ultramafic protolith in the mantle.

In the past, application of Os isotope studies of PGM from bedrock have been hampered for several reasons. First, PGM are relatively small (usually less than 10–20 μm; grains more than 50–100 μm are rare). It is difficult, therefore, to liberate them from bedrock in significant amounts. A reliable technique to quantitatively separate the PGM was lacking. However, liberation is needed to avoid uncertainties from excitation effects from host minerals (chromite, olivine, *etc*.) during Os isotope analysis. Developments in concentration techniques, including hydroseparation (Knauf 1996, Malitch *et al.* 2001b, 2002c, Malitch & Knauf 2002), and in Os isotope measurements of Os-rich alloys by N–TIMS (Creaser *et al.* 1991, Kostoyanov *et al.* 2000) and by *in situ* LA–MC–ICP–MS (Hirata *et al.* 1998, Junk 2001) now make it possible to obtain quantitative data on PGM grains.

Geological Setting and Sample Location

The Kraubath and Hochgrössen ultramafic massifs, situated within the Austrian province of Styria, have been interpreted as parts of a strongly deformed, metamorphosed and dismembered ophiolite complex presumably of Late Proterozoic to Early Paleozoic age (El Ageed *et al.* 1980, Stumpfl & El Ageed 1981, Neubauer 1988, Neubauer *et al.* 1989), that originated in a suprasubduction zone setting (Melcher *et al.* 1999b, 2002, Puhl 2000). Ultramafic and mafic rocks of the Hochgrössen massif are generally correlated with similar rocks in the Speik Complex located to the east, namely at Kraubath and Pernegg (Fig. 1B). However, Neubauer *et al.* (1989) have suggested that the ultramafic body at Hochgrössen might represent a separate unit not linked to the Speik Complex.

The Kraubath and Hochgrössen massifs are composed of metamorphosed, foliated harzburgite and dunite. Layers, lenses and stocks of coarse-grained orthopyroxenite ("bronzitite") are present at Kraubath only. A pre-Variscan (>400 Ma) high-pressure eclogite-facies metamorphic event has been recognized in the Hochgrössen massif only (Faryad *et al.* 2002); that massif subsequently underwent Variscan amphibolite and Alpine (~100 Ma) greenschist-facies conditions (Puhl 2000, Faryad & Hoinkes 2001). The pre-Variscan event has not been recognized at Kraubath yet, owing to a stronger Alpine amphibolite-facies imprint.

Numerous bodies of chromitite of generally small size (less than 0.5 m thick) are exposed in the northern part of the Kraubath and in the northwestern part of the Hochgrössen massifs. The chromitites are hosted by refractory dunite and harzburgite having preserved magmatic olivine (Mg# between 90 and 92, NiO in the range 0.3–0.5 wt.%) and orthopyroxene (Mg# between 91 and 93, <1 wt.% Al_2O_3), metamorphic talc, tremolite, serpentine, and chlorite. The host rocks are highly depleted in incompatible elements (Melcher *et al.* 1999b, 2002, Puhl 2000), displaying U-shaped *REE* patterns typical of highly depleted restitic mantle formed by multistage melting processes above supra-subduction zones (Parkinson & Pearce 1998, Monnier *et al.* 1999).

The predominant type of chromitite at Kraubath and Hochgrössen is schlieren, deformed stringers and streaks of massive chromite not more than a few centimeters thick. These are considered to be typical of podiform chromitite. The chemical composition of chromite at Kraubath varies in Cr# [$100^*Cr/(Cr + Al)$] from 80 to 86 and in Mg# [$100^*Mg/(Mg + Fe^{2+})$] from 44 to 50, whereas that at Hochgrössen varies in the Cr# range 74–84 and Mg# range 53–61. Since the first investigation of PGM in ophiolitic rocks of the Eastern Alps (Thalhammer & Stumpfl 1988), an increasing amount of information has been gathered on PGM in association with chromite together with whole-rock concentrations of the PGE (Thalhammer *et al.* 1990, Melcher & Mali 1998, Melcher *et al.* 1999b, Melcher 2000, Malitch *et al.* 2001b, d). These podiform occurrences of chromitite are distinct from banded chromitite, which has been recognized closely above the typical mantle section at Kraubath (Malitch 2001, Thalhammer *et al.* 2001, Malitch & Knauf 2002, Malitch *et al.* 2002c). The Os isotopic composition of PGM from the banded type of chromitite will be presented elsewhere (Malitch *et al.*, in prep.).

The PGM in three samples of podiform chromitite (sample HG 71 from Hochgrössen and samples K 137 and K 142 from Kraubath) were studied by LA–MC–ICP–MS. Sample HG 71 is a massive sample of podiform chromitite from an extensive outcrop in the northwestern part of the Hochgrössen massif. It consists of coarse-grained chromite that contains abundant inclusions of chlorite, Ni arsenide and Ni sulfide. A rim of magnetite around a core of chromite is common. Irregular thin veinlets and fractures in chromite filled with serpentine and chlorite result in a network-like secondary texture. Sample K 142 consists of unaltered massive chromitite (type 1) with a schlieren texture; it was taken from a small outcrop in the old chromite mine area south of the Sommergraben (Fig. 1 in Malitch *et al.* 2001b). Sample K 137 consists of massive chromitite; it was taken from the mine dumps of the same area. This chromitite is highly altered, with zones completely decomposed to talc and tremolite (type-2 chromitite).

Analytical Techniques

Bulk analyses of the chromitites for the PGE and Au were made in the Laboratory of Analytical Research and Monitoring of Mekhanobr-Analyt (St. Petersburg, Russia) using fire assay combined with chemical spectroscopy (for Pt, Pd, Rh, Ru, Ir, Au) and the kinetic method for Os (Alekseeva *et al.* 1978, Malitch 1990, Ushinskaya *et al.* 1999).

To constrain textural relationships of the Os-rich PGM with the associated minerals, all three samples of chromitite were first investigated optically. Ru–Os sulfides have been observed invariably as euhedral inclusions in chromite (Figs. 2a, b), thus revealing their primary signature. The chromitite samples were subsequently disintegrated by gradual milling followed by removal and sieving of the fine fraction (<90 μm). To avoid the possibility of artificial contamination from the mill, chromitite samples weighing 2–3 kg were first disintegrated to a grain-size fraction of <3 mm, and the

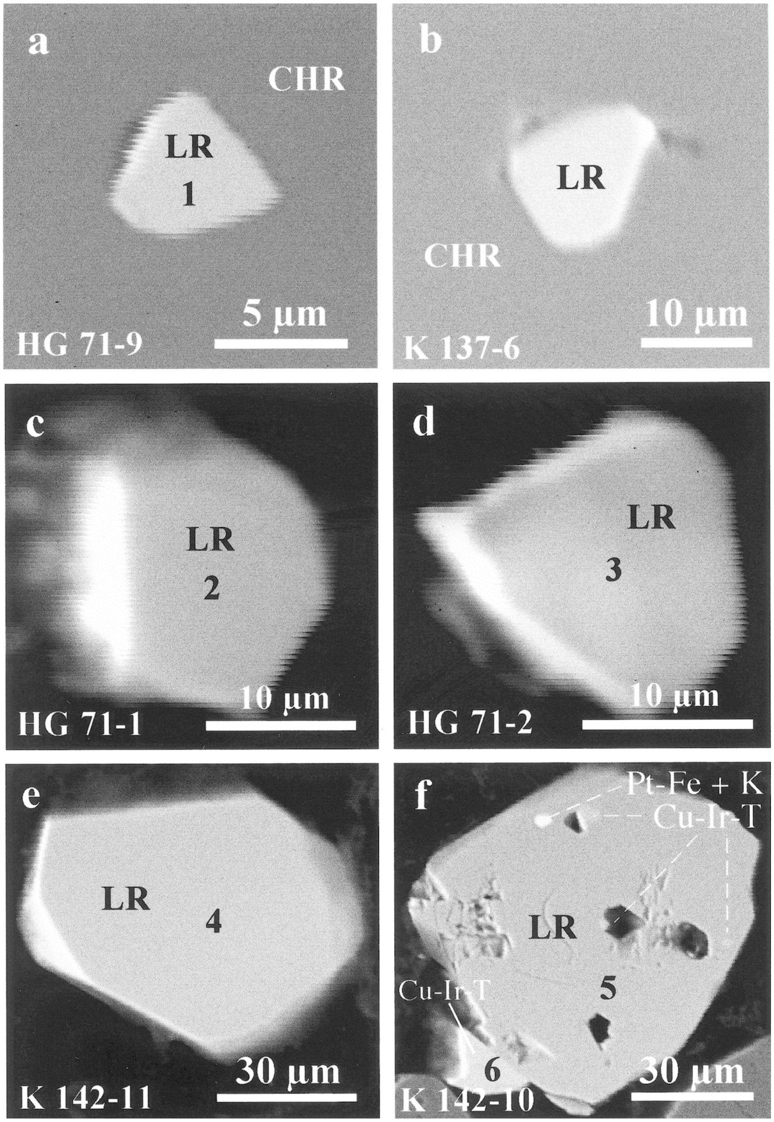

FIG. 2. Back-scattered electron images of euhedral single and polyphase PGM grains from podiform chromitite at Hochgrössen (a, c, d) and Kraubath (b, e, f). LR: laurite, (Os, Ir): iridian osmium; Pt–Fe: Pt–Fe alloy close to Pt_3Fe; K: keithconnite, Cu–Ir–T: cuproiridsite; CHR: chromite; numbers 1–6 denote areas of electron-microprobe analyses, and correspond to the same number in Table 1.

fraction <0.5 mm was removed from further concentration. The remaining 0.5–3 mm fraction was further disintegrated, and two fractions (*i.e.,* <37 µm and 37–90 µm) were separated. The heavy minerals (including PGM) of these two fractions were concentrated by a hydroseparation technique (Knauf 1996) at NATI Research JSC, St. Petersburg, Russia. Concentration factors between 4 × 10^4 to 1 × 10^5 times were attained. Finally, each concentrate with PGM was mounted in epoxy blocks and polished in separate sections for further detailed mineralogical and Os-isotope studies.

Chemical analyses were carried out with an ARL–SEMQ electron microprobe equipped with four wavelength-dispersion spectrometers (WDS) and with a LINK energy-dispersion analyzer (EDS) at the Institute of Geological Sciences (Department of Mineralogy and

Petrology), University of Leoben (Austria); analytical details are described in Malitch *et al.* (2001b).

After the microprobe analyses, the 16 grains of PGM from the Kraubath and Hochgrössen massifs were investigated by LA–MC–ICP–MS using a Microprobe II LA device (Thermo Elemental, Nd:YAG laser, 266 nm wavelength, up to 4 mJ per shot, 3 ns pulse width) and an AXIOM MC–ICP–MS (Thermo Elemental). All analyses were performed at the Technical University of Mining and Metallurgy (Institute of Archaeometry), Freiberg, Germany.

The ICP–MS was tuned using a desolvating nebulizer (MCN 6000, CETAC), a solution of 33 μg/L Re, 330 μg/L Os, and 330 μg/L Ir in 2% nitric acid, a nebulizer flow of 0.8 L/min Ar, and a radio frequency (RF) forward power of 1330 W. Helium was used as an ablation chamber gas, with a flow of 85 mL/min in a chamber 2.5 cm in diameter that has minimized dead volume. The air capacitor of the ICP–MS was optimized to obtain a RF reflected power of 12 to 18 W with this He addition to the plasma gas. Usually, it was necessary to stop the He flow to ignite the plasma of the AXIOM MC–ICP–MS. The remaining ICP parameters were optimized with the tune solution for signal stability and maximum signals during laser ablation of an Ir foil. The MC set-up, and corrections for Re and W contents, were checked with combined laser-ablation analyses of members of the ferberite–hübnerite series and the aerosol generated by the desolvating nebulizer, as described by Junk (2001).

Laser-ablation spots of 5 to 10 μm were used with a scan field that was adapted to the size of each sampling area, a laser-shot frequency of 20 Hz, and an energy output of up to 0.5 mJ. The energy output yielded power densities in the range of 10^9 to 10^{15} W/m^2. This corresponds to vaporization as the main process, using the model described by Steen (1991). Vaporization or phase explosion seemed to be able to generate smaller particles in contrast to ablation by a heating or melting process. Helium used as the ablation-chamber gas yielded a finer aerosol, and the redeposition of the ablated material near the ablation spot was minimized owing to the better thermal conductivity and, to a lesser extent, the lower density of He compared to Ar. Thus, the use of He as the ablation-chamber gas proved to be beneficial.

The aerosols generated by laser ablation were transported by a gas stream to the MC–ICP–MS (Thermo-Elemental Axiom, multicollector version with nine Faraday cup detectors, resolution 400). The signals were measured at *m/z* 183 (W), 184 (W + Os), 185 (Re), 186 (W + Os), 187 (Re + Os), 188 (Os), 189 (Os), 191 (Ir) and 193 (Ir) using the multichannel collector of the ICP–MS. The mass bias was corrected using an exponential fractionation law and the ^{188}Os/^{189}Os value. Isobaric interferences were very rare and were thus corrected using the natural abundances of Re or W. Molecular interferences and problems connected with the abundance sensitivity were checked for by using the ^{191}Ir/^{193}Ir value as a second possibility to corrected the mass bias, as described by Junk (2001). For the reported values, no significant contribution of these possible sources of error was detected. The abundances used for the calculations were published as best experimental values by Rosman & Taylor (1997).

Values of the isotope ratios are reported with experimental uncertainties that take into account the contributions of the Faraday cup efficiencies, the normalization values for mass-bias corrections using ^{188}Os/^{189}Os (Rosman & Taylor 1997), interference corrections, the signal noise, and the within-run standard deviations. The reported uncertainties are expanded uncertainties using a coverage factor of 2 which gives a level of confidence of approximately 95% (Ellison *et al.* 2000).

The use of within-run standard deviations or errors (*i.e.*, Pearson *et al*. 2002), which confirm that the IUPAC ^{188}Os/^{189}Os and ^{191}Ir/^{193}Ir values are within the experimental errors of the experiments, should be avoided. Such an approach does not include all sources of uncertainty, it only allows limited comparison among methods, and it lacks the traceability to SI units as required by DIN EN ISO/IEC 17025 (1999). The expanded uncertainty used in our study simplifies the comparison of isotope values determined by different methods or instruments.

PGE GEOCHEMISTRY AND PGE MINERALOGY

The Hochgrössen massif

Bulk concentrations of the PGE in podiform chromitite at Hochgrössen are low (in ppb): Os 77, Ir 10, Ru 88, Rh <5, Pt <6 and Pd <20. The rock thus has a negatively sloped chondrite-normalized PGE pattern, similar to those characteristic of ophiolite-type podiform chromitites (*e.g.*, Page & Talkington 1984, Barnes *et al.* 1985, Volchenko & Koroteev 1990).

Six solitary grains of laurite and two of Os–Ir alloy belong to PGM of the refractory IPGE-group (Figs. 2c, d). The PGM conform to the bulk-distribution pattern of the PGE expected and the predominance of Ru–Os sulfides and Os-rich alloys over other PGM reported from the mantle section of an ophiolite (Talkington *et al.* 1984, Legendre & Augé 1986, Augé & Johan 1988, Palandzhian *et al.* 1994, Melcher *et al.* 1997, Garuti *et al.* 1999).

The Kraubath massif

Bulk concentrations of the PGE and the PGM present in two samples of chromitite (K 142 and K 137) from the Sommergraben area of the Kraubath massif have been studied in detail by Malitch *et al.* (2001b) and are, thus, only briefly summarized here. Distribution patterns of PGE in these chromitites show considerable differences in the behavior of the less refractory PGE (PPGE group: Rh, Pt, Pd) compared to the refractory PGE

(IPGE group: Os, Ir, Ru). Platinum and Pd are more enriched in chromitite showing features of pronounced alteration (type 2, sample K 137). The unaltered chromitite (type 1, sample K 142) displays a negatively sloped chondrite-normalized PGE pattern typical of ophiolitic–podiform chromitite.

About 26 different PGM and two gold-rich minerals (*e.g.*, 21 PGM in type-1 chromitite and 13 PGM and two Au-rich minerals in type-2 chromitite) have been documented from a data base of 1117 PGM grains (Malitch *et al.* 2001b). Type-1 chromitite is dominated by laurite (43%), which occurs in complex polyphase assemblages with PGE alloys (Ir–Os, Os–Ir, Pt–Fe), PGE sulfides (kashinite, bowieite, cuproiridsite, cuprorhodsite, unnamed Ir-rich variety of ferrorhodsite, braggite, unnamed Ni–Fe–Cu–Rh and Ni–Fe–Cu–Ir sulfides) and Pd telluride (keithconnite). A variety of PGE sulfarsenides (33%) have been identified, including irarsite, hollingworthite, platarsite, ruarsite and a number of intermediate species, whereas sperrylite and stibiopalladinite are subordinate (2%). In contrast, type-2 chromitite is dominated by sperrylite (61% of all PGM), followed by PGE sulfarsenides (26%), Pd-rich minerals [*e.g.*, potarite (4.7%) and stibiopalladinite (3.5%)], Ru–Os sulfides (4%) and other PGM, which are present in minor amounts. The occurrence of such a wide variety of PGM is highly unusual for an ophiolitic environment. Three PGM assemblages have been recognized and attributed to processes ranging from magmatic to hydrothermal and weathering-related (Malitch *et al.* 2001b).

Chemical Composition of Os-Bearing Minerals

To avoid confusion with osmium and iridium as elements, we refer to the Os-rich alloy grains as iridian osmium (Os, Ir) and osmian iridium (Ir, Os). Members of the Ru–Os sulfide solid-solution series show a complete compositional spectrum, from laurite $(Ru,Os)S_2$ to erlichmanite $(Os,Ru)S_2$, whereas Ru–Os sulfarsenide is represented by ruarsite $(Ru,Os)AsS$. The composition of the Ru–Os sulfides, Os-rich alloys and PGE sulfarsenides, along with their morphology and details of their internal texture, are presented in Figures 2–4. The chemical composition of single PGM and polyphase PGM assemblages, which were measured by LA–MC–ICP–MS and N–TIMS, is given in Tables 1 and 2.

TABLE 1. REPRESENTATIVE RESULTS OF ELECTRON-MICROPROBE ANALYSES (WDS) OF PGE SULFIDES FROM THE KRAUBATH AND HOCHGRÖSSEN MASSIFS, AUSTRIA

No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Sample	HG	HG	HG	K	K	K	K	K	K	K	K	K	K	K
	71	71	71	142	142	142	137	142	142	142	142	142	142	137
	-9	-1	-2	-11	-10	-10	-121	-20	-95	-95	-9	-9	-6	-73
Mineral	Lrt	Lrt	Lrt	Lrt	Lrt	Cu-Ir-T	Lrt	Lrt	Lrt	Cu-Ir-T	Lrt1	Lrt2	Lrt	Erl
Figure	2a	2c	2d	2e	2f	2f	3a	3e	3f	3f	3g	3g	3h	
S wt.%	34.95	34.92	31.90	34.79	34.59	27.49	33.38	33.66	34.52	27.21	34.07	34.97	34.99	29.60
As	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.89	0.91	0.93	0.00	0.19	2.58	0.00	0.29	0.16	0.70	0.20	0.22	0.34	0.00
Ni	0.00	0.00	0.00	0.00	0.00	1.42	0.00	0.00	0.00	1.95	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	6.87	0.00	0.00	0.00	7.90	0.00	0.00	0.00	0.00
Ru	44.35	42.00	28.36	39.80	39.98	0.00	35.63	40.42	42.51	0.00	38.93	44.63	45.09	19.92
Rh	0.00	0.22	2.13	1.36	1.42	9.78	0.00	0.00	1.95	11.23	0.52	0.90	0.82	0.00
Pd	0.95	0.68	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Os	16.27	19.40	30.90	15.88	16.74	0.00	28.17	19.61	14.01	0.00	21.77	17.24	15.89	45.70
Ir	2.21	2.48	5.45	8.43	7.53	49.42	3.20	5.67	6.53	48.35	4.11	0.90	1.69	4.07
Pt	0.00	0.00	0.00	0.00	0.00	2.26	0.00	0.00	0.00	2.49	0.00	0.00	0.00	0.00
Total	99.62	100.61	99.67	100.26	100.45	99.82	100.38	99.65	99.52	99.83	99.60	98.86	98.82	99.29
S at.%	66.04	66.24	66.17	67.00	66.65	61.26	66.81	66.13	66.19	60.95	66.74	66.48	66.4	66.82
As	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.97	0.99	1.11	0.00	0.21	3.30	0.00	0.33	0.18	0.90	0.22	0.24	0.37	0.00
Ni	0.00	0.00	0.00	0.00	0.00	1.73	0.00	0.00	0.00	2.39	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	7.72	0.00	0.00	0.00	8.93	0.00	0.00	0.00	0.00
Ru	26.57	25.27	18.66	24.31	24.43	0.00	22.62	25.19	25.85	0.00	24.19	26.92	27.14	14.26
Rh	0.00	0.13	1.37	0.82	0.85	6.79	0.00	0.00	1.16	7.84	0.32	0.54	0.48	0.00
Pd	0.54	0.39	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Os	5.18	6.20	10.80	5.16	5.44	0.00	9.50	6.49	4.53	0.00	7.19	5.53	5.08	17.39
Ir	0.70	0.78	1.89	2.71	2.42	18.37	1.07	1.86	2.09	18.07	1.34	0.29	0.53	1.53
Pt	0.00	0.00	0.00	0.00	0.00	0.83	0.00	0.00	0.00	0.92	0.00	0.00	0.00	0.00
Ru#	84	80	63	83	82		70	80	85		77	83	84	45

Numbers 1-13 refer to analysis points on Figures 2 and 3, respectively. Columns 1-3: samples from Hochgrössen, columns 4-14: samples from Kraubath. Symbols: Lrt: laurite, Lrt 1 and Lrt 2: coexisting (intergrown) compositions of laurite, Cu-Ir-T: cuproiridsite, Erl: erlichmanite. Ru# = 100 Ru/ (Ru + Os).

TABLE 2. REPRESENTATIVE RESULTS OF ELECTRON-MICROPROBE ANALYSES (WDS) OF Os-Ir ALLOYS AND PGE SULFARSENIDES FROM THE KRAUBATH AND HOCHGRÖSSEN MASSIFS, AUSTRIA

No.	15	16	17	18	19	20	21	22	23	24	25	26
Sample	HG 71 -3	K 142 -32	K 137 -121	K 137 -121	K 137 -83	K 142 -5	K 142 -5	K 142 -5	K 142 -20	K 142 -9	K 142 -9	K 142 -6
Mineral	(Os,Ir)	(Ir,Os)	Rua	RuNiAsS	Rua	Rua	Irs	Rua-Plt	Irs	Plt-Rua	Irs	Irs
Figure		4b**	3a	3a	3c	3d	3d	3d	3e	3g	3g	3h
S wt.%	0.00	0.00	14.06	15.38	13.86	14.69	13.07	14.32	12.19	13.25	13.06	12.53
As	0.00	0.00	34.46	30.92	32.60	34.97	25.95	29.89	24.43	30.18	26.83	25.25
Fe	0.68	0.62	0.19	0.00	0.26	0.24	0.00	0.00	0.20	0.15	0.00	0.25
Ni	0.00	0.00	0.24	15.80	0.40	0.31	0.00	3.19	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ru	1.30	0.32	28.29	35.69	30.24	40.16	5.62	14.26	0.90	11.69	2.66	3.42
Rh	0.00	3.09	0.00	0.00	0.00	0.00	1.22	1.95	4.78	6.99	6.46	1.98
Pd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Os	59.91	24.23	19.33	0.00	18.98	8.83	0.46	1.46	0.00	4.65	0.69	0.00
Ir	37.97	68.89	1.97	2.51	1.89	1.93	48.55	17.05	57.57	9.81	45.66	50.23
Pt	0.00	3.05	0.24	0.00	0.00	0.00	3.55	18.32	0.00	24.45	5.00	4.96
Total	99.86	100.20	98.78	100.30	98.23	101.13	98.42	100.44	100.07	101.17	100.36	98.62
S at.%	0.00	0.00	33.76	31.41	33.57	33.00	37.24	35.73	35.71	34.35	36.33	36.45
As	0.00	0.00	35.41	27.01	33.79	33.63	31.65	31.91	30.62	33.48	31.93	31.44
Fe	2.27	2.03	0.26	0.00	0.36	0.31	0.00	0.00	0.34	0.22	0.00	0.42
Ni	0.00	0.00	0.31	17.62	0.53	0.38	0.00	4.35	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ru	2.39	0.58	21.56	23.11	23.24	28.62	5.08	11.29	0.84	9.61	2.35	3.16
Rh	0.00	5.51	0.00	0.00	0.00	0.00	1.08	1.51	4.36	5.64	5.60	1.79
Pd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Os	58.59	23.34	7.82	0.00	7.75	3.34	0.22	0.61	0.00	2.03	0.32	0.00
Ir	36.75	65.68	0.79	0.85	0.76	0.72	23.07	7.09	28.13	4.24	21.18	24.37
Pt	0.00	2.86	0.09	0.00	0.00	0.00	1.66	7.51	0.00	10.43	2.29	2.37

Columns 17-26 refer to analysis points on Figure 3. Column 15: sample from Hochgrössen; columns 16-26: samples from Kraubath. Symbols of PGM: (Os,Ir): iridian osmium, (Ir,Os): osmian iridium, Rua–Plt and Plt–Rua: uncommon ruarsite–platarsite solid-solution series, RuNiAsS: unnamed Ru-Ni sulfarsenide, Irs: irarsite. **Composition 16 refers to osmian iridium shown in Malitch et al. (2001b).

Laurite–erlichmanite series

At Kraubath, the Ru–Os sulfides, in which Ru# [100 Ru/(Ru + Os)] varies from 95 to 26, are dominated by laurite, documented both in single and polyphase grains, whereas Os-rich sulfide (erlichmanite) is less common (Table 1, Figs. 2b, e, f, 3a–h, 4a, b). Laurite from podiform chromitite at Hochgrössen has values of Ru #, ranging from 84 to 63 (Table 1, Figs. 2a, c, d, 4a). The composition of the laurite–erlichmanite series, plotted on the Os–Ir–Ru diagram (Figs. 4a, b), shows common Ru substitution for Os. Laurite usually carries moderate concentrations of both Ir and Rh, whereas erlichmanite contains a notable abundance of Ir only (Table 1). The wide compositional trend recorded at Kraubath is similar to that of Ru–Os sulfide inclusions from chromitites at Kempirsai and Rai-Iz, Urals (Melcher *et al.* 1997, Garuti *et al.* 1999), whereas the more restricted compositional range of laurite at Hochgrössen is in good agreement to that of laurite inclusions reported by Thalhammer & Stumpfl (1988) and Thalhammer *et al.* (1990).

Os–Ir alloy

The Os–Ir alloy occurs in a polyphase assemblage with laurite, Pt–Fe alloy and Ir–Os alloy at Kraubath, and as single euhedral grains at Hochgrössen. The Ir–Os alloy is typical of unaltered podiform chromitite at Kraubath only (Malitch *et al.* 2001b, 2002c). Compositions of Os–Ir and Ir–Os alloys cluster at both sides of the miscibility gap defined by Harris & Cabri (1991) in the Os–Ir–Ru diagram. The Os–Ir alloy contains low concentrations of Fe (2.10–2.38 at.%) and Ru (2.30–2.49 at.%), whereas the Ir–Os alloy carries significant concentrations of Rh (up to 5.51 at.%) and Pt (up to 2.86 at.%) (Table 2, anal. 15 and 16, respectively).

The PGE sulfarsenides

The PGE sulfarsenides at Kraubath are commonly associated with Ru–Os sulfides and show complex, and in some cases unconventional substitutions (Malitch *et al.* 2002c, this study, Table 2). Such phenomena are exemplified by several grains (Figs. 3a, d, g, 4c–f, Table

1, anal. 7, 11, 12; Table 2, anal. 17, 18, 20–22, 24, 25); grain K 137–121 shows the association of at least four minerals [laurite (Ru# 70), ruarsite (Ru# 73), unnamed Ru–Ni sulfarsenide (possibly a solid-solution series of ruarsite–gersdorffite) and Ru-rich oxide], whereas grains K 142–5 and K 142–9 reveal associations of three different PGE sulfarsenides [ruarsite (Ru# 90), irarsite and Pt–Ru–Rh sulfarsenide] and two distinct compositions of laurite (Ru# 83 and 77, respectively) associated with two PGE sulfarsenides (irarsite and Pt–Ru sulfarsenide), respectively.

The PGE sulfarsenides are dominated by irarsite (Figs. 3d, e, g, h, 4e) and Ru–Pt sulfarsenide (Figs. 3d, g, 4f) followed by ruarsite and hollingworthite (Figs.

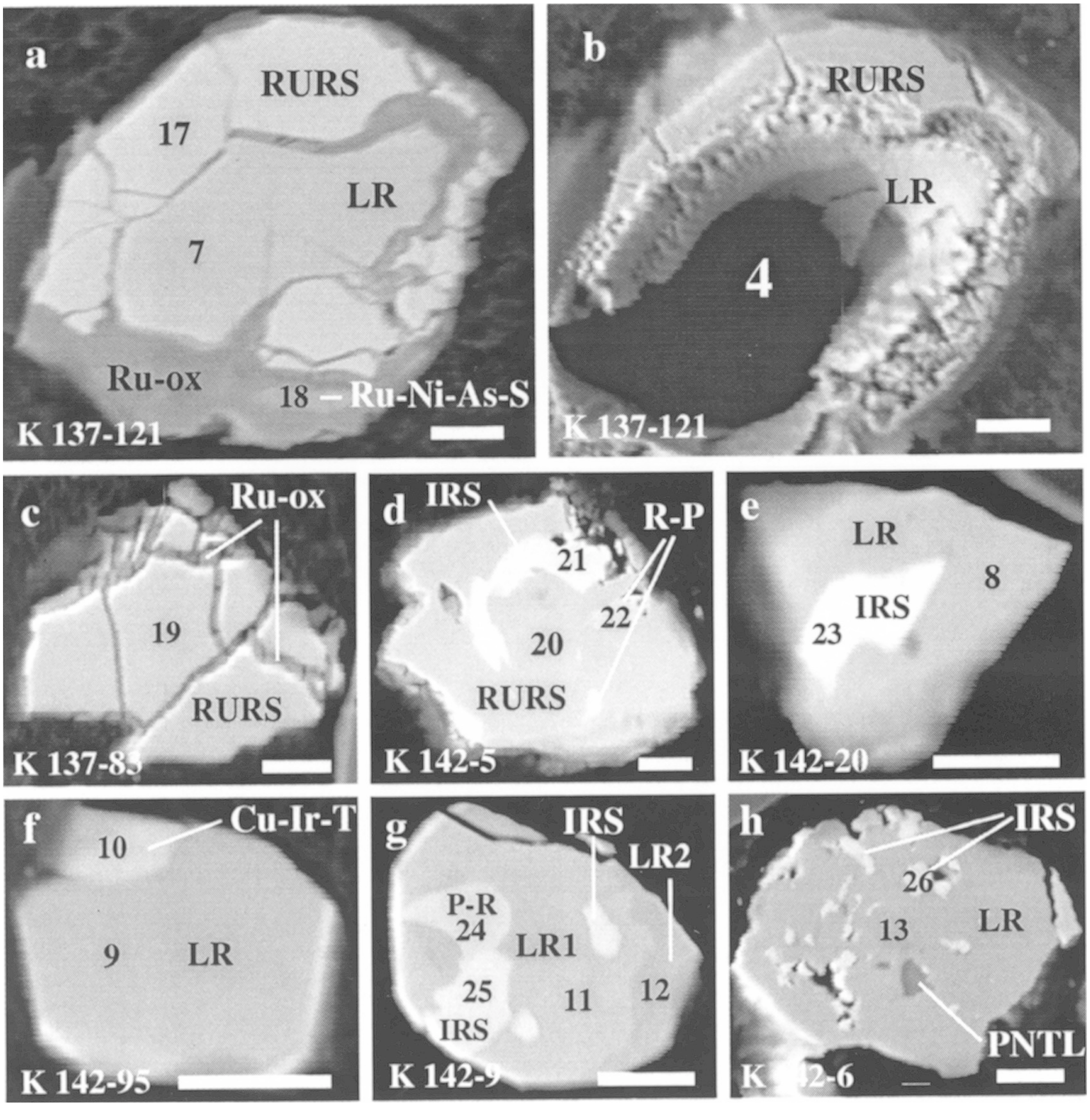

FIG. 3. Back-scattered electron images of PGM assemblages from the Kraubath massif before (a, c–h) and after (b) laser ablation MC–ICP–MS. LR, LR 1 and LR 2: laurite, RURS: ruarsite, IRS: irarsite, R–P and P–R: members of the uncommon ruarsite–platarsite series, Cu–Ir–T: cuproiridsite, Ru–ox: Ru oxide(?), Ru–Ni–As–S: unnamed Ru–Ni sulfarsenide, PNTL: pentlandite. Numbers 7–13 and 17–26 denote areas of electron-microprobe analyses corresponding to the same numbers in Tables 1 and 2, respectively. Number 4 in black hole (Fig. 3b) indicate the area of the laser-ablation MC–ICP–MS analysis, which corresponds to the same number in Table 3. Scale bar is 10 μm

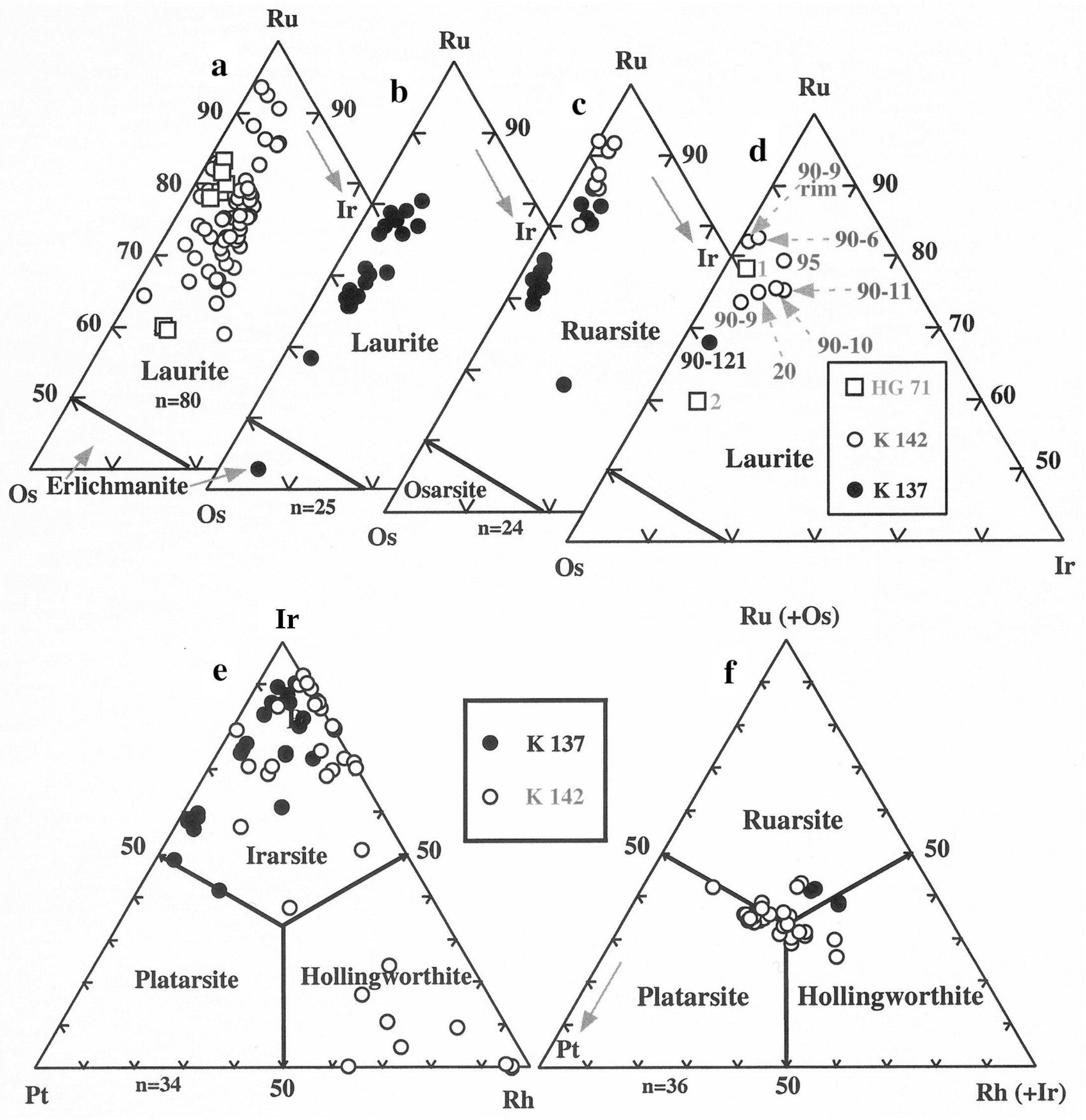

FIG. 4. Composition of Ru–Os sulfides (a, b and d) and ruarsite (c) in the triangular diagram Ru–Os–Ir (at.%) and various PGE sulfarsenides in the diagrams Rh–Ir–Pt (e) and Ru + Os–Pt–Rh + Ir (f) from podiform chromitites at Kraubath (samples K 137 and K 142) and Hochgrössen (sample HG 71).

3a, c, d, 4c, e). Ruarsite (Table 2, anal. 17, 19, 20) shows common Ru-for-Os substitution (up to 19.33 wt.% Os), and Ru # varies from 90 to 73. Minor elements detected in ruarsite include Ir, Ni and Fe (up to 1.97, 0.40 and 0.26 wt.%, respectively).

OSMIUM-ISOTOPE DATA

The ^{187}Os/^{188}Os values of PGM from podiform chromitites at Kraubath and Hochgrössen are listed in Table 3 and shown in Figure 5. Since the concentration of Re in all samples appears to be less than 0.05 wt.%, the isotopic effect caused by *in situ* radioactive decay of ^{187}Re is negligible. Consequently, the value of ^{187}Os/^{188}Os in the PGM corresponds to that in the source at the time of PGM formation. The ^{187}Os/^{188}Os value in laurite from Kraubath and Hochgrössen varies between 0.11940 ± 0.00059 and 0.12437 ± 0.00050; the ^{187}Os/^{188}Os value in ruarsite at Kraubath ranges from 0.12105 ± 0.00158 to 0.12299 ± 0.00027 (Table 3, Fig. 5; the expanded uncertainties correspond to the 95% confidence interval). The dispersion of $^{187}Os/^{188}Os$ values in various PGM from samples K 142 and HG 71 exceeds the analytical uncertainty (Fig. 5). Therefore, isotopic fractionation among the majority of PGM is significant and similarly expressed in both massifs. For instance, the range of the Os isotopic composition of PGM at Kraubath measured by LA–MC–ICP–MS is from 0.12026 ± 0.00088 to 0.12437 ± 0.00050 (Table 3, Fig. 5, samples K 142 and K 137), closely matching that at Hochgrössen (Table 3, Fig. 5, sample HG 71). However, two Ru–Os sulfides from sample K 142 (grains K 142–11 and K 142–10, Figs. 2e, f) measured by N–TIMS (Malitch 2001) do not show significant variation and provide the most unradiogenic $^{187}Os/^{188}Os$ values, 0.1158 ± 0.0007 to 0.1162 ± 0.0004 (Fig. 5). An even narrower range of $^{187}Os/^{188}Os$ values (from 0.12105 ± 0.00158 to 0.12117 ± 0.00014) characterizes PGM grains from the highly altered chromitite (Table 3, anal. 3 and 4, Figs. 3a–c, 5, sample K 137). These PGM grains are less radiogenic than the majority of the PGM from typical podiform chromitite (Fig. 5, samples K 142 and HG 71). Examples of primary and secondary PGM associations, which show unradiogenic Os isotope compositions, are represented by the grains K 137–121 (Figs. 3a, b) and K 137–83 (Fig. 3c) from highly altered chromitite. Apart from primary laurite, the first one contains secondary PGM [unnamed Ru–Ni sulfarsenide and Ru-rich oxide], whereas in the second one, ruarsite is rimmed and cross-cut by Ru-rich oxide. Unradiogenic $^{187}Os/^{188}Os$ values of PGM grains from highly altered chromitite (sample K 137) indicate that the Re–Os system in Os-bearing minerals (laurite and ruarsite) from these assemblages has remained unchanged, despite a secondary metamorphic overprint. The stability of the Os isotope system at the single-crystal scale has also been demonstrated for detrital 3.0–4.0 Ga old Os-rich alloys and gold from the Evander and Klerksdorp goldfields at Witwatersrand, South Africa (Malitch *et al.* 2000, 2001a, Kirk *et al.* 2001).

Since the $^{187}Os/^{188}Os$ values in all analyzed PGM do not exceed the value of the contemporary undifferentiated mantle material (CHUR) (0.12863 ± 0.00046, Chen *et al.* 1998), a model Re–Os age can be calculated according to the method of Allègre & Luck (1980). In order to calculate model (mantle-derived) ages of PGM,

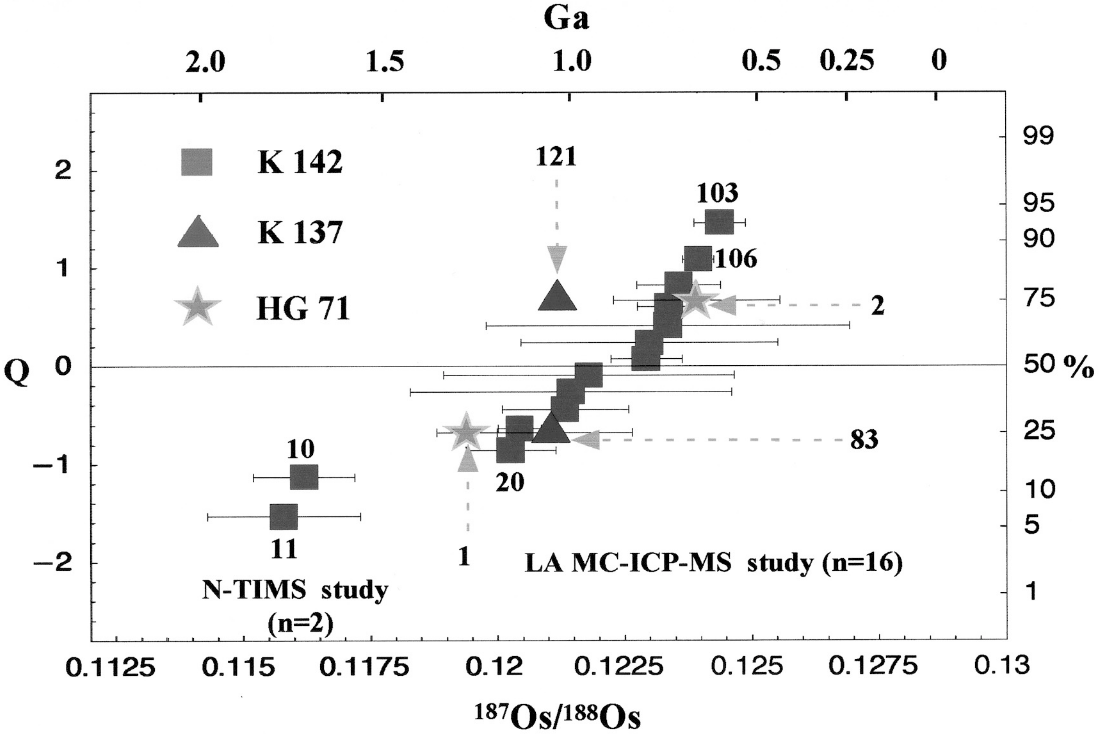

FIG. 5. Normal probability plot of $^{187}Os/^{188}Os$ and model age values of PGM from podiform chromitites at Kraubath and Hochgrössen. N–TIMS data (PGM grains K 142–11 and K 142–10) from Malitch (2001) also are included. Sum probability is defined as (i–1/*n*)/*n* for the ith sample out of *n*; quantile Q is calculated using normal distribution and sum probability. The expanded uncertainty for each PGM is also indicated.

the $^{187}Os/^{188}Os$ evolution curve of the mantle has to be known and constrained by initial and present-day $^{187}Os/^{188}Os$ values. In this study, we are using the primary and contemporary $^{187}Os/^{188}Os$ values (0.12863 ± 0.00046 and 0.0953 ± 0.0013, respectively) for an undifferentiated mantle reservoir (CHUR) as estimated by Chen *et al.* (1998). Alternative $^{187}Os/^{188}Os$ values for the present-day mantle, in widespread use for calculation of model ages, are 0.12736 (Yin *et al.* 1996), 0.1270 (Shirey & Walker 1998) and 0.1296 ± 0.0008 (Meisel *et al.* 2001). Calculations using the latter would result in model ages that are approximately 0.2 Ga older. However, as is clear from recent studies on BM sulfides (Alard *et al.* 2001a, b, 2002), the latter estimate cannot be considered a valid proxy material for mantle sulfides. Since most ultramafic rocks from oceanic upper mantle follow the chondritic evolution curve (Snow & Reisberg 1995), we favor the initial and present-day $^{187}Os/^{188}Os$ estimates for chondrites (Chen *et al.* 1998), which are considered to be more reliable for the dating of primary PGM from the mantle section of an ophiolite.

The wide range of $^{187}Os/^{188}Os$ values of different Os-bearing PGM (*e.g.*, laurite and ruarsite) from the Kraubath massif results in Re-depletion ages in the range of 1147 to 584 Ma (Table 3, LA–MC–ICP–MS study, n = 16), if the equation for the calculation of $^{187}Os/^{188}Os$ model ages is used: $(0.12863 - {}^{187}Os/{}^{188}Os_{sample})/0.0073$ (Ga). The Os isotopic composition of two grains of laurite at Hochgrössen yielded model ages of 1264 Ma and 645 Ma, which is in accordance with the total variation defined by those at Kraubath (Table 3, Fig. 5, samples HG 71 and K 142, respectively). In contrast, model $^{187}Os/^{188}Os$ ages for PGM from the highly altered chromitite vary between 1038 and 1022 Ma only (Table 3, Fig. 5, sample K 137). The Os isotope system thus has not been disturbed during later thermal events, which affected both massifs in pre-Variscan, Variscan and Alpine times (Puhl 2000, Faryad & Hoinkes 2001, Faryad *et al.* 2002).

TABLE 3. LASER-ABLATION MC–ICP–MS Os ISOTOPE DATA ON PGM FROM PODIFORM CHROMITITES AT KRAUBATH AND HOCHGRÖSSEN, AUSTRIA

	Massif sample	Figure	Mineral assemblage, Ru number	$^{187}Os/^{188}Os$	$\gamma Os_{t=0}$	t Ga
			Kraubath			
1	K 142-20	Fig. 3e	Lrt (80), Irs	0.12026 ± 0.00088	-6.51	1.147
2	K 142-15		Lrt (77)	0.12044 ± 0.00042	-6.37	1.122
3	K 137-83	Fig. 3c	Rua (75), Ru oxide (?)	0.12105 ± 0.00158	-5.89	1.038
4	K 137-121	Fig. 3a	Lrt (70), Rua (73), Ru oxide (?)	0.12117 ± 0.00014	-5.80	1.022
5	K 142-14		Lrt (88)	0.12133 ± 0.00124	-5.68	1.000
6	K 142-9	Fig. 3g	Lrt1 (77), Lrt2 (83), Irs, Pt–Ru sulfarsenide	0.12145 ± 0.00089	-5.58	0.984
7	K 142-6	Fig. 3h	Lrt (84), Irs, Pn	0.12180 ± 0.00064	-5.31	0.936
8	K 142-101		Lrt (88)	0.12292 ± 0.00070	-4.44	0.782
9	K 142-5	Fig. 3d	Rua (90), Irs, Ru–Pt sulfarsenide	0.12299 ± 0.00027	-4.38	0.773
10	K 142-70		Lrt (82)	0.12335 ± 0.00357	-4.10	0.723
11	K 142-100		Lrt (83)	0.12337 ± 0.00061	-4.09	0.721
12	K 142-95	Fig. 3f	Lrt (85), Cui	0.12357 ± 0.00081	-3.93	0.693
13	K 142-106		Lrt (95), unnamed Ni–Rh–(Fe–Cu–Ir) sulfide	0.12395 ± 0.00030	-3.64	0.641
14	K 142-103		Lrt (80), Irs	0.12437 ± 0.00050	-3.31	0.584
			Hochgrössen			
15	HG 71-1	Fig. 2c	Lrt (80)	0.11940 ± 0.00059	-7.18	1.264
16	HG 71-2	Fig. 2d	Lrt (63)	0.12392 ± 0.00164	-3.66	0.645

The parameter $\gamma Os_{t=0}$ is the percent deviation of the isotopic composition of a PGM compared with the average composition of a chondritic mantle at present: $\gamma Os_{(t=0)} = ({}^{187}Os/{}^{188}Os_{sample}/0.12863 - 1)*100$, where 0.12863 is the present-day isotopic composition of the undifferentiated mantle reservoir (Chen *et al.* 1998); number in bracket refers to the Ru number [100*Ru/(Ru + Os)] of laurite or ruarsite, respectively. Symbols: Lrt laurite, Irs irarsite, Rua ruarsite, Cui cuproiridsite, Pn pentlandite.

Discussion

Podiform chromitites within residual mantle from an ophiolite complex are generally well characterized based on geological, geochemical and mineralogical grounds (*e.g.*, Lago *et al.* 1982, Dick & Bullen 1984, Talkington *et al.* 1984, Legendre & Augé 1986, Prichard *et al.* 1986, Augé 1987, Augé & Johan 1988, Prichard & Tarkian 1988, McElduff & Stumpfl, 1990, Nilsson 1990, Volchenko & Koroteev 1990, Lord 1991, Palandzhian *et al.* 1994, Melcher *et al.* 1997, Garuti *et al.* 1999, Ohnenstetter *et al.* 1999, Bai *et al.* 2000). Most podiform chromitites show negatively sloped chondrite-normalized PGE patterns, which are mineralogically expressed by the preponderance of a rather limited variety of PGM of the IPGE group (*i.e.*, dominated by laurite or Ru–Os–Ir alloy). Rarely documented positive chondrite-normalized PGE patterns in podiform chromitites are usually ascribed to secondary processes leading to remobilization and reconcentration of the PPGE (*e.g.*, Thalhammer *et al.* 1990, Malitch *et al.* 2001b).

Extensive Os isotopic data on Proterozoic ophiolite occurrences based on chromite concentrates and chromitites have been reported by Walker *et al.* (1996) and Tsuru *et al.* (2000). Os isotopic analyses for Phanerozoic ophiolites reported by Meisel *et al.* (1997), Melcher *et al.* (1999a) and Walker *et al.* (2002) have been restricted to a limited number of chromite-rich samples from the mantle portion or lower crustal sequence (or both) within a particular ophiolite locality studied. The present study provides new constraints on the osmium isotopic composition of the oceanic upper mantle based on extensive dataset of Ru–Os sulfides and sulfarsenides from variably altered podiform chromitites of the Speik Complex within the Eastern Alps.

Main PGM assemblages in mantle environments

The dominance of Ru–Os sulfides or Os-rich alloys over other PGM is not unusual in mantle sections of dunite–harzburgite and lherzolite ultramafic complexes. In fact, it is considered a typical feature of PGE occurrences in dunite–harzburgite and lherzolite complexes worldwide (*e.g.*, Stumpfl 1974, Cabri & Harris 1975, Legendre & Augé 1986, Augé & Johan 1988, Dmitrenko *et al.* 1990, Palandzhian *et al.* 1994, Cabri *et al.* 1996, Torres-Ruiz *et al.* 1996, Nakagawa & Franco 1997, Garuti *et al.* 1999, Melcher 2000). However, the

Kraubath massif is characterized by a high diversity of PGM assemblages (Malitch 2001, Malitch *et al.* 2001b, 2002c, Thalhammer *et al.* 2001, Malitch & Knauf 2002). The occurrence of about 35 different PGM and Au-rich minerals documented from only three bedrock samples of chromitite is uncommon for an ophiolitic environment. Such unusual diversity is due to the application of a new technique of concentration applied for variously altered and distinctly different chromitites of the Kraubath massif. The relative abundance of PGM in podiform chromitite at Hochgrössen corresponds well to that in mantle-hosted chromitites as reported elsewhere (*e.g.*, Tamvatnei, Russia: Dmitrenko *et al.* 1990; Krasnogorsky, Russia: Palandzhian *et al.* 1994; Ojen, Spain: Torrez-Ruiz *et al.* 1996; Kempirsai, Kazakhstan: Melcher *et al.* 1997; Rai–Iz, Russia: Garuti *et al.* 1999; Ust'–Bel'sky, Russia: Rudashevsky *et al.* 1999).

The composition of Ru–Os sulfides from podiform chromitite (Figs. 4a, b) is close to the wide compositional range for the laurite–erlichmanite series of mantle-hosted chromitites (Garuti *et al.* 1999, and references cited therein). A broad spectrum of element substitutions is also characteristic of PGE sulfarsenides at Kraubath and Hochgrössen (Thalhammer & Stumpfl 1988, Thalhammer *et al.* 1990, Melcher 2000, Malitch *et al.* 2001b, 2002c, this study). These PGM are represented by (1) irarsite, platarsite and hollingworthite (Fig. 4e), all of which have cubic symmetry (space group: $Pa3$) and commonly form extensive solid-solution among end members, (2) Ru–Os sulfarsenide, namely ruarsite (Fig. 4c), characterized by monoclinic symmetry (space group: $P2_1/c$), and (3) Pt–Ru sulfarsenide, which shows an uncommon solid-solution between cubic PGE sulfarsenide (*e.g.*, platarsite, hollingworthite and irarsite) and monoclinic ruarsite (Fig. 4f). Similar complex PGE sulfarsenides have been reported from a number of dunite–harzburgite and lherzolite complexes worldwide (*e.g.*, Shetland, United Kingdom: Prichard *et al.* 1986, Prichard & Tarkian 1988; Osthammeren, Norway: Nilsson 1990; Ojen, Spain: Torres-Ruiz *et al.* 1996). Such PGE sulfarsenides commonly exhibit a complex intergrowth (Figs. 3d, g), and also are associated with laurite or sperrylite (Figs. 3a, e, g, h).

Mineralogical and Os isotopic constraints for the source of the PGE mineralization

We assume that the primary PGM, generally exhibiting equilibrium assemblages, formed early as part of the chromite precipitation event, similar to what has been suggested by Talkington *et al.* (1984), Augé & Johan (1988), Melcher *et al.* (1997), Garuti *et al.* (1999) among others. Mineralogical evidence from podiform chromitite at Kraubath and Hochgrössen suggests that the PGM were trapped partly as solids (*i.e.*, single grains of laurite or Os–Ir alloy, and polyphase grains containing PGE alloys + laurite) as well as in the liquid state (other polyphase PGM).

The Os isotope compositions of PGM from Kraubath and Hochgrössen correspond to those estimated for the mantle and mantle peridotites, which have relatively low $^{187}Os/^{188}Os$ values as a result of evolution in a low Re/Os environment (*e.g.*, Hattori & Hart 1991, Luck & Allègre 1991, Martin 1991, Snow & Reisberg 1995, Shirey & Walker 1998). However, the Os isotopic compositions are somewhat different from that of laurite measured by N–TIMS (Fig. 5) and from the whole-rock Os isotopic composition of chromite concentrates from chromitites at Kraubath and Hochgrössen (Meisel *et al.* 1997, Melcher *et al.* 1999b). The fact that the Ru–Os sulfides from sample K 142 measured by N–TIMS do not show significant variation may be due to the limited number of PGM grains studied ($n = 2$), a statement that is also valid for the two PGM grains from highly altered chromitite (sample K 137) measured by LA–MC–ICP–MS. It is noteworthy that these grains (K 137–121 and K 137–83) contain secondary PGM that have been attributed to late overprinting events at Kraubath (Malitch *et al.* 2001b). If, therefore, the Re–Os system was perturbed, then the PGM would be expected to yield the most radiogenic values. However, the PGM grains from highly altered chromitite (Table 3, Fig. 5, sample K 137) are less radiogenic than many other samples of laurite from typical podiform chromitite (Table 3, Fig. 5, samples K 142 and Hg 71). In contrast, two whole-rock $^{187}Os/^{188}Os$ values determined on chromite from podiform chromitite at Kraubath and Hochgrössen (Meisel *et al.* 1997) and ten $^{187}Os/^{188}Os$ values determined on chromite concentrates at Kraubath (Melcher *et al.* 1999b) closely match either present-day depleted MOR mantle (DMM) or an enriched mantle source (*e.g.*, 0.1239–0.1271 and 0.1329–0.2028, respectively). Thus, Os isotopic data obtained on chromite concentrates of the Kraubath and Hochgrössen massifs tend toward more radiogenic values compared to results for PGM obtained by N–TIMS (Malitch 2001) and LA–MC–ICP–MS studies. The high degree of Os isotopic heterogeneity obtained implies that comprehensive sets of Os isotope data (*e.g.*, on PGM, chromite, chromitite, *etc.*) will be needed to provide better understanding of Os isotopic behavior in the ophiolitic mantle. Therefore, a restricted number of Os isotope analyses, especially obtained on whole rocks from a particular ophiolite occurrence (Walker *et al*. 2002), should be treated with caution since these can lead to ambiguous interpretations.

The early formation of Os-rich minerals at high temperatures implies that the Os isotopic composition of laurite and ruarsite reflects that of the source region in the mantle. Therefore, the low $^{187}Os/^{188}Os$ values, corresponding to the Os isotopic composition of the mantle, indicate a common subchondritic mantle source for the PGE. Furthermore, the unradiogenic $^{187}Os/^{188}Os$ values of laurite and ruarsite are similar to those of detrital Os-rich alloys derived from other dunite–harzburgite and lherzolite complexes worldwide (Hattori & Hart 1991, Hattori *et al.* 1992, Hattori & Cabri 1992, Lyon *et al.* 1997, Hirata *et al.* 1998, Bird *et al.* 1999, Ohnenstetter *et al.* 1999, Rudashevsky *et al.* 1999, Malitch *et al.* 2002b, Meibom & Frey 2002, among others). For instance, the bedrock laurite and ruarsite from the Eastern Alps, Austria and the detrital Os-rich alloys derived from several other dunite–harzburgite and lherzolite complexes (*e.g.*, the Kunar Complex, Taimyr Peninsula, and the Ust'–Bel'sky Complex, Far East, both in Russia, and the Klamath Mountains, California and Oregon, U.S.A.) have a wide range of subchondritic $^{187}Os/^{188}Os$ values (0.1094–0.1259, *n* = 67, Fig. 6) and $\gamma Os_{t=0}$ values (*e.g.*, from –14.95 to –2.12, *n* = 67). On the contrary, the range of $^{187}Os/^{188}Os$ and the γOs values in PGM derived from clinopyroxenite–dunite complexes (also known as zoned, Uralian, Alaskan or Aldan type) are distinctly different from those observed in dunite–harzburgite complexes, as pointed out by Malitch *et al.* (2002a). Indeed, PGM derived from the Guli, Kondyor and Inagli clinopyroxenite–dunite complexes (Siberian Craton, Russia) show a narrow range of subchondritic $^{187}Os/^{188}Os$ values (*e.g.*, 0.12432–0.12520, *n* = 30), consistent with a single-stage process of PGE concentration in these complexes and with a significant metallogenic potential of their parent ultramafic protoliths (Malitch 1999, Malitch *et al.* 2001c, 2002a, Malitch & Badanina 2002, Malitch & Thalhammer 2002).

A wide scatter of osmium isotope compositions of laurite and ruarsite is in obvious disagreement with present-day $^{187}Os/^{188}Os$ estimates for various mantle reservoirs [*i.e.*, chondritic mantle (CHUR) 0.12736 (Yin *et al.* 1996) or 0.1270 (Shirey & Walker 1998), depleted upper MOR mantle (DMM) 0.1246 (Snow & Reisberg 1995), convecting upper mantle 0.12809 (Walker *et al.* 2002), and primitive upper mantle (PUM) 0.1296 (Meisel *et al.* 2001)]. Our results suggests that the $^{187}Os/^{188}Os$ value for the ophiolitic upper mantle, deduced from bedrock PGM, lies within the range of 0.1158–0.12437 (*n* = 18).

Os isotopic age constraints and geodynamic implications

With rare exceptions (Kusky *et al.* 2001), most ophiolites worldwide are considered to be younger than

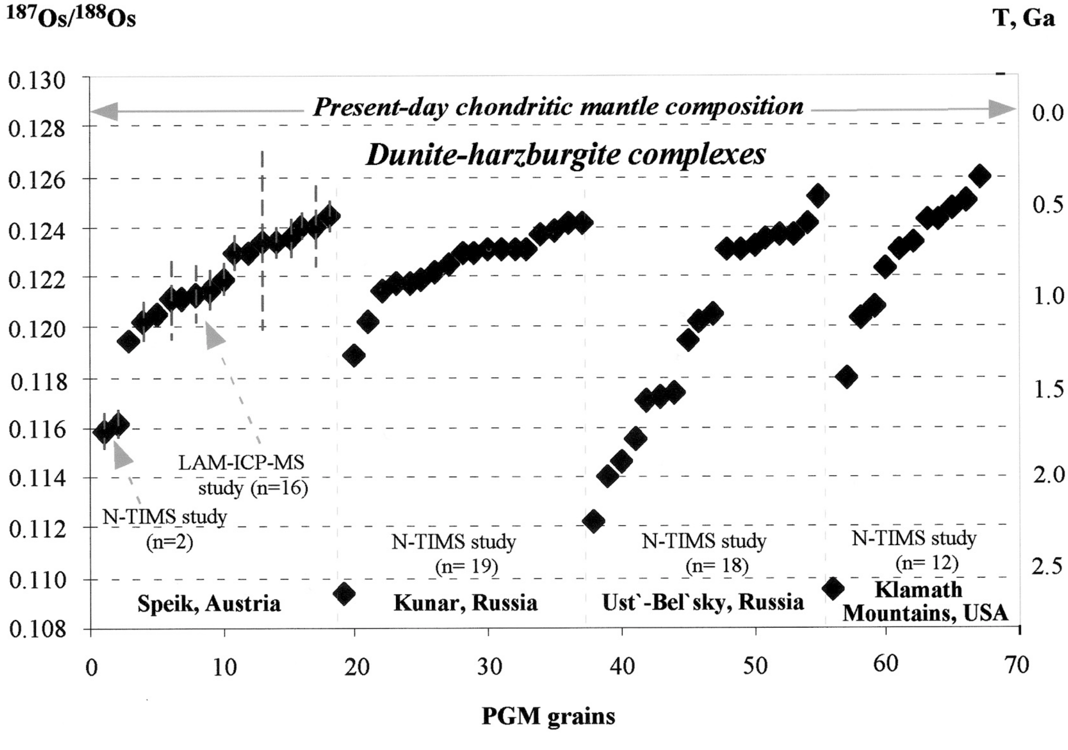

FIG. 6. Os isotopic composition of PGM from ophiolite-type complexes. LA–MC–ICP–MS data: this study. N–TIMS data are taken from Malitch (2001) for PGM from Speik, from Malitch *et al.* (2002b) for PGM from Kunar, from Rudashevsky *et al.* (1999) for PGM from Ust'–Bel'sky, and from Meibom & Frei (2002) for PGM from the Klamath Mountains. Error bars are shown in cases where expanded uncertainty exceeds the size of the diamond symbol.

1 Ga. Their ages of formation show distinct peaks in the Late Proterozoic (Late Riphean), Cambro-Ordovician and Jurassic-Cretaceous (Abbate *et al.* 1985, Nicolas 1989, Ishiwatari 1994). The similarity of the Kraubath and Hochgrössen massifs to an ophiolite has been recognized by El Ageed *et al.* (1980) and Stumpfl & El Ageed (1981). Consequently, these massifs have been interpreted as strongly metamorphosed Early Paleozoic or Precambrian dismembered ophiolites, emplaced during Variscan nappe tectonics (Neubauer 1988, Neubauer *et al.* 1989). The Speik Complex rests tectonically on the Core Complex (Fig. 1b), a Late Proterozoic to Early Paleozoic magmatic arc assemblage, which underwent a complex polyphase metamorphic evolution. Metamorphism was polyphase, including (1) pre-Variscan (older than 400 Ma) eclogite facies (700°C, >1.5 GPa) documented in mafic rocks at Hochgrössen (Faryad *et al.* 2002), (2) Variscan amphibolite facies, and (3) early Alpine (~100 Ma) greenschist facies (Puhl 2000, Faryad & Hoinkes 2001). Metamorphism was accompanied by pervasive flow of fluid along faults and fissures.

The age of the ultramafic protoliths in the Speik Complex is still poorly constrained. Recent attempts using whole-rock analyses (Sm–Nd and Re–Os systematics) of ultramafic rocks of the Speik Complex gave errorchron "ages" ranging from about ~780 Ma for the harzburgites to ~550 Ma for intrusive orthopyroxenites, respectively (Fig. 12 in Melcher *et al*. 2002, Melcher & Meisel, submitted). Suprachondritic ^{187}Os/^{188}Os values (^{187}Os/^{188}Os$_{(I)}$ = 0.178 ± 0.003) characteristic of orthopyroxenites are different from subchondritic ^{187}Os/^{188}Os values of the harzburgites hosting them (0.12270–0.12578). On the basis of these results, a two-stage scenario has been proposed (Melcher *et al*. 2002): (1) partial melting of undepleted mantle during the Late Proterozoic resulted in formation of residual harzburgite in a mid-ocean ridge system or evolved back-arc basin; (2) second-stage melting in a supra-subduction-zone setting during the Early Cambrian led to the formation of a highly depleted residual mantle (harzburgites and dunites) and mantle-derived melts, from which the orthopyroxenites formed.

Our age estimates on the formation of the ultramafic protoliths in the Eastern Alps, based on osmium isotopic composition of PGM (N–TIMS and LA–MC–ICP–MS studies), yielded model ages in the range of 1758 to 584 Ma, assuming a chondritic mantle reservoir (CHUR) (Figs. 5, 6). Furthermore, U–Pb(Th) model ages of highly radiogenic uraninite (U,Pb,Th)O_2 from banded chromitite, which occurs above the mantle section at Kraubath, vary from 1400 to 1200 Ma (Malitch *et al.*, in prep.). These Re–Os and U–Pb model ages are indicative of the existence of a Precambrian parent ultramafic protolith, which most likely formed during the Late Proterozoic.

The unradiogenic ^{187}Os/^{188}Os values of laurite and ruarsite from podiform chromitites at Kraubath and Hochgrössen (0.11580–0.12437, *n* = 18, N–TIMS and LA–MC–ICP–MS studies) provide isotopic evidence for locally restricted but temporally extended periods of PGM formation. The Os isotopic composition of these PGM indicates that they record much older melting events than would be expected from single-stage melting of undepleted mantle. As one of the possible explanations of this phenomenon, the PGM remained isolated from the convecting upper mantle after their formation. In this case, peridotites of the Speik complex are not simple residues after partial melting at a mid-ocean ridge system or evolved back-arc in the Late Proterozoic. Instead, they may represent a mixture of (1) refractory isolated blocks that retain much older ages and (2) ultramafic rocks formed during a partial melting episode (~780 Ma). A similar scenario has been advocated by Parkinson *et al*. (1998) and Snow & Schmidt (1999) for the Izu–Bonina–Mariana and Zabargad peridotites, respectively. Furthermore, Os isotope model ages of PGM at Kraubath are older than the time of formation of orthopyroxenite (~550 Ma), implying that subduction zones indeed may represent graveyards for ancient oceanic lithosphere, as proposed by Parkinson *et al*. (1998).

On the other hand, another option to interpret the results obtained would be to consider the mantle source, from which the PGM were derived, as much less radiogenic than presently assumed. Within this scenario, Os isotope heterogeneity might also reflect the effect of variable degrees of partial melting of this mantle source. Finally, the origin of this heterogeneity may be also attributed to the presence of subcontinental lithospheric mantle (SCLM), characterized by unradiogenic ^{187}Os/^{188}Os values [*i.e.*, <0.1220 (Handler *et al.* 1997) or <0.1160 (Nägler *et al.* 1997)], which has been lately incorporated into asthenospheric mantle with more radiogenic ^{187}Os/^{188}Os values [*i.e.*, 0.1220–0.1230 (Snow & Reisberg 1995, Shirey & Walker 1998)].

In our opinion, the wide range of subchondritic ^{187}Os/^{188}Os values of PGM (*e.g.*, laurite, ruarsite and Os-rich alloys) derived from the dunite–harzburgite complexes worldwide (Fig. 6) is consistent with a model in which a prolonged history of melting events of parent ultramafic source-rocks took place in the mantle. The Os isotopic system of PGM thus unequivocally records multiple events in the chemical differentiation history of the Eastern Alpine mantle relics, represented by the mantle sections at Kraubath and Hochgrössen. We further propose that substantial heterogeneity among the unradiogenic ^{187}Os/^{188}Os values is a feature typical of PGM from the mantle section of an ophiolite. Consequently, suprachondritic ^{187}Os/^{188}Os values (*i.e.*, >0.12863), which also have been detected in detrital PGM grains (*e.g.*, Hattori & Hart 1991, Rudashevsky *et al.* 1999, Meibom & Frey 2002) could indicate derivation from a distinct source other than dunite–harzburgite sequences from the mantle section of an ophiolite. Most conceivable sources for such PGM would be the transition zone or crustal sequence of an ophiolite. Once extensive Os isotopic data on bedrock PGM from ophiolites of different age (*i.e.*, Proterozoic, Paleozoic, Mesozoic, Cenozoic) become available, a more plausible explanation could be developed.

Finally, Os isotope systematics suggest that melt-depletion event(s) recorded by unradiogenic $^{187}Os/^{188}Os$ values at Kraubath and Hochgrössen and certain other peridotite occurrences worldwide (*e.g.*, Hattori & Hart 1991, Parkinson *et al.* 1998, Snow & Schmidt 1999, Malitch & Kostoyanov 1999, Brandon *et al.* 2000, Malitch *et al.* 2002a; Fig. 6) are older than the time of their emplacement in the crust. This observation is similar to some extent to the phenomenon recorded by Re–Os isotopes in sulfide inclusions in diamonds (Spetsius *et al.* 2002).

CONCLUSIONS

1. A combination of the unique dataset on PGM, obtained by a combination of various techniques of separation and concentration (including the hydroseparation method), and osmium isotope study (LA–MC–ICP–MS and NTI–MS), has allowed us for the first time to measure relatively small PGM grains from bedrock and unequivocally to determine the Os isotopic source of PGE-mineralization in podiform chromitites of Eastern Alpine mantle sections. Podiform chromitites at Kraubath and Hochgrössen are characterized by unradiogenic $^{187}Os/^{188}Os$ and $\gamma Os_{t=0}$ values, indicative of a subchondritic mantle source of the PGE. These values yield a very wide range of $^{187}Os/^{188}Os$ (0.11580 to 0.12437) and γOs (–9.97 to –3.31) values, which is almost identical to the Os isotope composition of detrital Os-rich alloys derived from other ophiolite-type ultramafic massifs. The unradiogenic $^{187}Os/^{188}Os$ values, combined with the high degree of Os isotopic heterogeneity documented, are considered a typical feature of the mantle section of an ophiolite.

2. Calculated $^{187}Os/^{188}Os$ model ages of laurite and ruarsite, assuming a chondritic mantle reservoir (CHUR), vary from 1758 to 584 Ma. Therefore, they likely indicate the existence of a Precambrian ultramafic protolith. The range of model ages for PGM at Kraubath is in basic accordance with that for PGM at Hochgrössen. The Os isotopic evidence supports the assumption of a genetic link between the ultramafic protoliths for the Kraubath and Hochgrössen dunite–harzburgite bodies as parts of the Speik Complex.

3. The Os isotope results show that the Re–Os system in PGM remained unchanged from the time of formation of the PGM until now, despite later thermal events affecting both massifs. The evidence of long-lived osmium isotope heterogeneity obtained implies that comprehensive sets of Os isotope data can only provide a valid understanding of Os isotopic behavior in the ophiolitic upper mantle. Therefore, a restricted number of Os isotope analyses should be treated with caution. Finally, we infer that the Os isotopic composition of PGM can be employed to test the validity of various petrological models.

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