

First LA MC-ICP-MS Study of Ru-Os Sulfides from Podiform and Banded Chromitites at Kraubath and Hochgrössen, Austria: Os Isotopic Evidence for Two Contrasting Sources

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Introduction

Primary platinum-group minerals (PGM) are promising targets to avoid ambiguity in the interpretation of Os-isotopic results in ultramafic rocks. The advantage of the Re-Os system, applied to Os-rich minerals, is that PGM contain osmium as a main or trace element, while at the same time almost lack Re. This feature permits accurate initial Os isotope ratios to be determined, assuming that the Os isotopic composition of PGM has not changed after their formation and, therefore, reflects that of the source. Ru-Os sulfides and alloys are frequently the earliest precipitates in ultramafic systems. Consequently, these PGM are potentially the best tracers of mantle melting events, which may be unequivocally recognised during ultramafic protolith(s) formation.

However, Os isotopic compositions of Ru-Os sulfides from bedrock in ophiolites are scarce. To fill this gap and to demonstrate the high potential of Os isotopes measured in bedrock PGM a detailed laser ablation (LA) and multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS) study of 18 Os-bearing PGM grains, both single and polyphase, has been conducted. PGM, comprising laurite (Ru,Os) S_2 , erlichmanite (Os,Ru) S_2 and ruarsite (Ru,Os)AsS, were liberated from podiform and banded chromitites of the Kraubath (Malitch et al. 2001b,c; Malitch and Knauf, 2002) and Hochgrössen (present study) dunite-harzburgite massifs, the largest mantle relicts in the Eastern Alps, Austria.

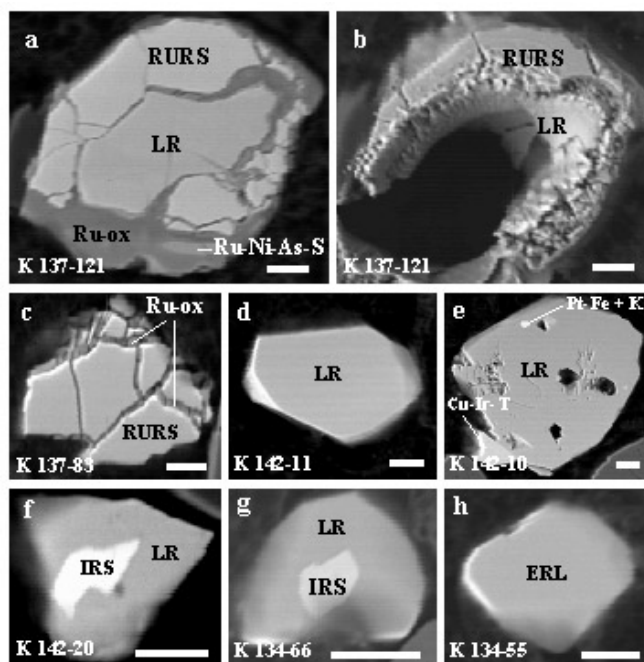


Figure 1. Back scattered electron images of euhedral single and polyphase PGM grains from distinct chromitites at Kraubath before (a, c-h) and after (b) laser ablation MC-ICP-MS. LR – laurite, RURS - ruarsite, Ru-ox - Ru oxide(?), Ru-Ni-As-S - unnamed Ru-Ni sulfarsenide, Pt-Fe - Pt-Fe alloy, K - keithconnite, Cu-Ir-T - cuproiridsite, IRS - irarsite, ERL - erlichmanite. Black hole (Fig. 1b) refers to the area of laser ablation MC-ICP-MS analysis. Scale bar is 10 μ m.

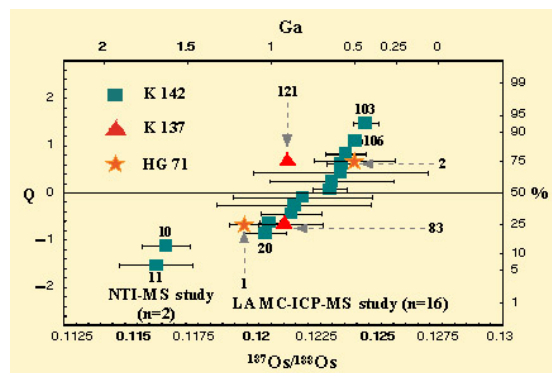


Figure 2. Normal probability plot of $^{187}\text{Os}/^{188}\text{Os}$ values and model ages of PGM from podiform chromitites at Kraubath and Hochgrössen. NTI-MS data (PGM grains K 142-11 and K 142-10) from Malitch (2001) are also included. The expanded uncertainty for each PGM is also indicated.

Geology and Sample Location

The Kraubath and Hochgrössen ultramafic massifs have been interpreted as parts of a dismembered Late Proterozoic to Early Palaeozoic, strongly deformed and metamorphosed ophiolite complex (Stumpfl and El Ageed, 1981; Neubauer et al., 1989), which originated in a supra-subduction setting (Melcher, 2000). The Kraubath and Hochgrössen massifs are composed of metamorphosed, and 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 metamorphic event has been recognized in the Hochgrössen massif, which subsequently underwent Variscan amphibolite and Alpine (100 Ma) greenschist facies conditions (Melcher, 2000).

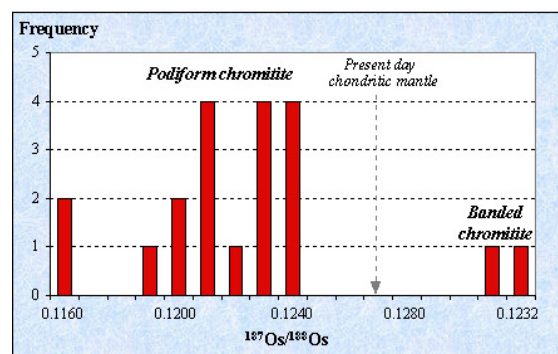


Figure 3. Histogram of Os isotopic composition of Ru-Os sulfides and sulfarsenides from distinct chromitites at Kraubath and Hochgrössen

PGM, studied by LA MC-ICP-MS analysis, are exemplified by 4 chromitite samples (sample HG 71 from Hochgrössen and samples K 134, 137 and K 142 from Kraubath). Sample HG 71 is a massive podiform chromitite from an extensive outcrop in the northwestern part of the Hochgrössen massif. Sample K 142 is an unaltered massive chromitite (podiform type 1) with podiform textures (schlieren-type) from a small outcrop in the old chromite mine area south of the Sommergraben, while sample K 137 is a massive chromitite from the mine dumps of the same area (Fig. 1 in Malitch et al. 2001b). This chromitite is highly altered with zones completely decomposed to talc and tremolite (podiform type 2 chromitite). These podiform chromitite occurrences are distinct from a banded chromitite (sample K 134), which has been recognised closely above the typical mantle section at Kraubath (Malitch, 2001; Malitch et al., 2001c).

Analytical Techniques

Whole rock platinum-group element (PGE) analyses for chromitites were obtained 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. To constrain textural relationships of Os-rich PGM with associated minerals, all chromitite samples (HG 71, K 134, K 137 and K 142) were first investigated in polished sections. Ru-Os sulfides are present as euhedral inclusions enclosed in chromite, thus revealing their primary signature. Chromitite samples were, then, disintegrated and the heavy minerals (including PGM) were concentrated by a hydroseparation technique at NATI Research JSC, St. Petersburg, Russia, by reaching concentration factors between 4×10^4 to 1×10^5 times. Finally, each concentrate with PGM was mounted in epoxy blocks and polished in separate sections for further detailed mineralogical and Os-isotopic studies. Analytical details of these techniques are described in Malitch et al. (2001b).

After microprobe analysis, the 18 PGM grains were investigated by LA MC-ICP-MS at the Technical University of Mining and Metallurgy (Institute of Archaeometry), Freiberg, Federal Republic of Germany. LA was performed with a Microprobe II laser ablation device (VG, Nd: YAG laser, 266 nm, pulse duration 3 ns, energy output to sample up to 4 mJ, ablation spot size up to 50 μm , Fig. 1b). The aerosols generated by LA were transferred by a He stream to the MC-ICP-MS (ThermoElemental Axiom, multicollector version with 9 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). Technical details of the method and principal factors that influence the accuracy of LA MC-ICP-MS analyses are presented elsewhere (Junk, 2001 and references cited therein).

PGE Concentrations and PGE mineralogy

Whole rock PGE concentrations in podiform chromitite at Hochgrössen are low (in ppb): Os 77, Ir 10, Ru 88, Rh <5, Pt <6 and Pd <20. This results in a negatively sloped chondrite-normalized PGE pattern, similar to those characteristic of ophiolite-type podiform chromitites. Eight PGM grains documented in this sample are represented by solitary grains of laurite (75 %) and Os-Ir alloy (25 %), which belong to PGM of the refractory IPGE-group only. These PGM are in good accordance with the bulk PGE distribution pattern, and common dominance of Ru-Os sulfides and IPGE alloys over other PGM in the mantle section of an ophiolite. Whole rock PGE concentrations and PGE mineralogy of three chromitite samples (K 134; K 137 and K 142) from the Sommergraben area of the Kraubath massif have been studied in detail (Malitch, 2001; Malitch et al., 2001b, c; Malitch and Knauf, 2002). At Kraubath, Os-bearing PGM (laurite, erlichmanite, ruarsite and Os-rich alloys) occur as (a) single grains and (b) complex polyphase assemblages (Fig. 1).

Osmium Isotope Data

The $^{187}\text{Os}/^{188}\text{Os}$ values of PGM from distinct chromitites at Kraubath and Hochgrössen are presented in Figures 2 and 3. Os isotope composition of Ru-Os sulfides from banded chromitite at Kraubath (i.e. erlichmanite K134-55 and laurite, K 134-66, Fig. 1g, h) yield the highest $^{187}\text{Os}/^{188}\text{Os}$ (0.13080 \pm 0.00011 and 0.13212 \pm 0.00065, respectively) and $\gamma\text{Os}_{(T=0)}$ (2.70 to 3.73) values, compared to the 'unradiogenic' $^{187}\text{Os}/^{188}\text{Os}$ values of laurite and ruarsite from podiform chromitite (Fig. 3). Indeed, the $^{187}\text{Os}/^{188}\text{Os}$ ratio in laurite from Kraubath and Hochgrössen varies between 0.11940 \pm 0.00059 and 0.12437 \pm 0.00050; $^{187}\text{Os}/^{188}\text{Os}$ in ruarsite at Kraubath ranges from 0.12105 \pm 0.00158 to 0.12299 \pm 0.00027 (Fig. 2, the expanding uncertainties correspond to the 95%-confidence interval). The dispersion of $^{187}\text{Os}/^{188}\text{Os}$ values in different PGM from samples K 142 and HG 71 exceeds the analytical uncertainty. Therefore, isotopic fractionation among most Os-bearing minerals is significant and similarly expressed in both massifs. For instance,

the $^{187}\text{Os}/^{188}\text{Os}$ values of PGM at Kraubath, measured by LA MC-ICP-MS, range from 0.12026 \pm 0.00088 to 0.12437 \pm 0.00050 (Fig. 2, samples K 142 and K 137). They are similar to those from Hochgrössen (Fig. 2, sample HG 71). However, two Ru-Os sulfides from sample K 142 (grains K 142-11 and K 142-10, Fig. 1d, e), measured by NTI-MS (Malitch, 2001), do not show significant variation and provide the lowest $^{187}\text{Os}/^{188}\text{Os}$ values of 0.1158 \pm 0.0015 to 0.1162 \pm 0.0010 (Fig. 2). An even more narrow range of $^{187}\text{Os}/^{188}\text{Os}$ values (e.g., from 0.12105 \pm 0.00158 to 0.12117 \pm 0.00014) characterises PGM grains from the highly altered chromitite (Figs. 1a-c, 2, sample K 137). These PGM grains are less radiogenic than most of the PGM from typical podiform chromitite (Fig. 2, 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 (Fig. 1a, b) and K 137-83 (Fig. 1c) 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 (?). Low $^{187}\text{Os}/^{188}\text{Os}$ values of PGM grains from highly altered chromitite (sample K 137) indicate that the Re-Os system for laurite and ruarsite from these assemblages has remained unchanged, despite secondary metamorphic overprint. The stability of the Os isotope system at the mineral level has also been demonstrated for detrital 3.0-4.0 Ga old Os-rich alloys from the Evander goldfield at Witwatersrand, South Africa (Malitch et al., 2001a). Age estimates on the formation of the ultramafic protoliths in the Eastern Alps, based on osmium isotopic composition of PGM from podiform chromitite, yield model ages in the range of 1685 to 436 Ma, assuming chondritic mantle reservoir (Fig. 2).

Discussion and Conclusions

A combination of the unique PGM data set, obtained during various concentration techniques (including hydroseparation method), and Os-isotope study (LA MC-ICP-MS and NTI-MS) permits, for the first time, the measurement of relatively *small* monophase PGM grains and the determination of two contrasting isotopic sources of PGE mineralizations from distinct chromitites of Eastern Alpine mantle sections (Fig. 3). Podiform chromitites at Kraubath and Hochgrössen are characterised by 'unradiogenic' $^{187}\text{Os}/^{188}\text{Os}$ and γOs values, indicative of a chondritic to subchondritic mantle source of PGE. These values yield a very wide range of $^{187}\text{Os}/^{188}\text{Os}$ (0.11580-0.12437, n=18,

NTI-MS and LA MC-ICP-MS data) and $\gamma\text{Os}_{(T=0)}$ (-9.08 to -2.35). The Os-isotopic composition of PGM from altered chromitite at Kraubath (sample K 137) is similar or even less radiogenic than that from typical podiform chromitite (K 142). This suggests that the Re-Os system within PGM has not been disturbed during later thermal events.

Os-isotope composition of laurite and ruarsite from podiform chromitite at Kraubath and Hochgrössen provides further evidence for a residual origin of ultramafic rocks from the mantle section of an ophiolite. These data are consistent with the model, in which prolonged history of melting events of parent ultramafic source rocks took place in the subchondritic mantle. In contrast, erlichmanite and laurite from banded chromitite at Kraubath show high $^{187}\text{Os}/^{188}\text{Os}$ (0.13080 ± 0.00011 to 0.13212 ± 0.00065) and $\gamma\text{Os}_{(T=0)}$ (2.70 to 3.73) values, indicative of a suprachondritic source of PGE (Fig. 3). This signature might be interpreted as either evidence of an enriched mantle source or an indication of a radiogenic crustal component, which was introduced during a subduction-related event postulated by Melcher (2000). Os isotopic evidence is in good agreement with distinct origin of chromitites, proposed on the basis of geological, geochemical and mineralogical data (Malitch, 2001; Malitch et al., 2001c; Malitch and Knauf, 2002). Finally, the high Os-isotopic heterogeneity obtained imply that comprehensive sets of Os isotope data can only provide a valid understanding of Os-isotopic behaviour in the ophiolitic mantle. Therefore, a restricted number of Os-isotope analyses, especially obtained on whole rocks from ophiolites, should be treated with caution.

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