Diversity of PGM Assemblages at Kraubath: A Case Study of Mantle-Derived Chromitites from the Eastern Alps, Austria

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Introduction

Podiform and stratiform chromitites are generally well defined, based on distinct geological, geochemical and mineralogical features. Podiform chromitites usually represent discordant, relatively small bodies in residual dunites and harzburgites from the mantle section of ophiolites, whereas stratiform chromitites are concordant sheet-like bodies in the upper crustal section of ophiolite suites. However, there is a significant gap of information on the "*in between* ", the Moho transition zone, which divides mantle and crustal sections of ophiolites (Boudier and Nicolas, 1995).

Furthermore, in many examples, and especially at Kraubath, a clear mismatch can be demonstrated between total platinum-group element (PGE) concentrations in chromitites and the PGE mineralogy as observed in polished thin sections (Thalhammer et al., 1990; Melcher, 2000). Therefore, another approach of clarifying the mineralogical siting of PGE in different chromitites was used (Malitch et al., 2001; this study). As a result, noble metal inventory of the Kraubath massif has been doubled and now contains a total of 35 (Table 1). This contribution summarizes new compositional data on banded chromitite, which occurs as a band in a stratigrafically higher position than the typical podiform chromitites from the mantle section of the Kraubath massif. In order to demonstrate the compositional difference between the banded and podiform chromitites, PGE mineralogy from both chromitite types is discussed along with their whole rock PGE concentrations.

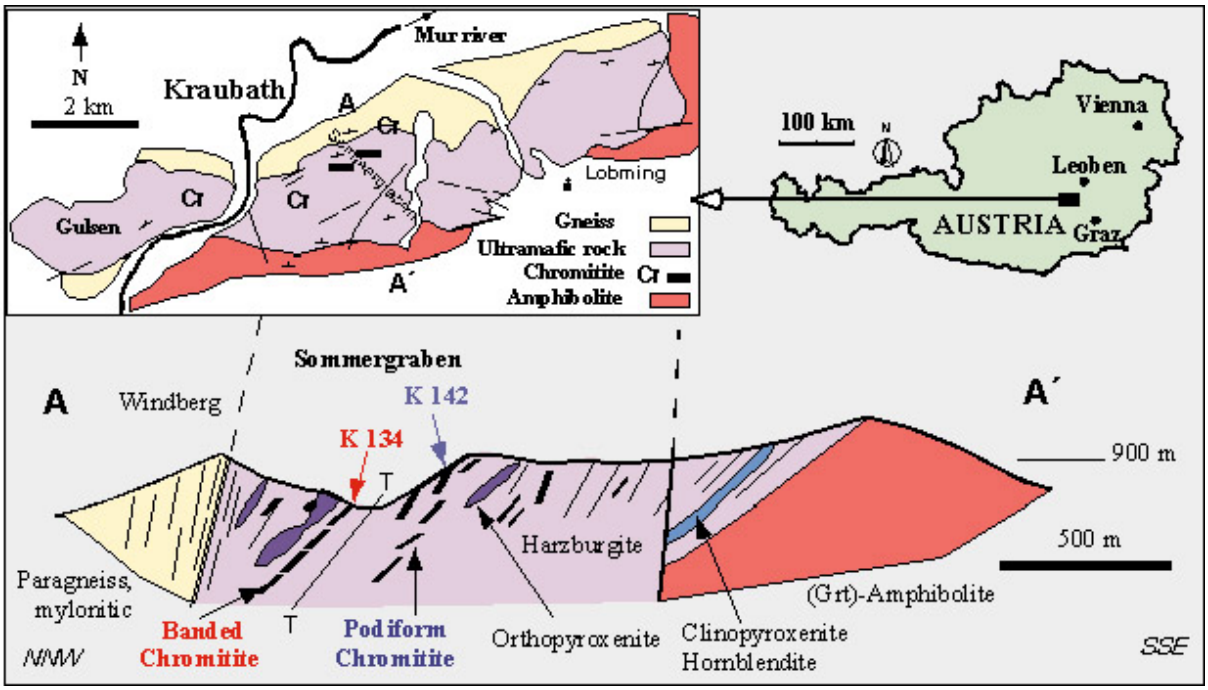

Figure 1. *Simplified geological map and cross-section (A-A´) through the Kraubath dunite-harzburgite massif, showing the location of banded and podiform chromitites in the Sommergraben area. Thickness of chromitite and orthopyroxenite is not to scale. T-T inferred lower boundary for the Moho transition zone. Sample locations for K 134 and K 142 are also indicated.*

Table 1. *Noble metal minerals in distinct chromitites from the Kraubath Massif.*

Mineral	Podiform		Banded
	1	This study	
Laurite $(Ru,Os)S_2$	• (35)	• (90)	• (6)
Erlichmanite $(Os,Ru)S_2$	• (8)		• (3)
Kashinite $(Ir,Rh)_2S_3$		• (3)	
Bowieite $(Rh,Ir)_2S_3$		• (1)	
Cuproiridsite $CuIr_2S_4$		• (4)	
Cuprorhodsite $CuRh_2S_4$		• (2)	
Unnamed $(Fe,Cu)(Ir,Rh)_2S_4$		• (3)	
Unnamed $(Ni,Fe,Cu,Ir,Rh)_2S_3$		• (3)	
Unnamed (Ni,Fe,Cu,Rh)S		• (4)	
Braggite (Pt,Pd)S		• (2)	
Ruthenium (Ru,Os,Ir)	• (1)		
Osmium (Os,Ir)		• (1)	• (1)
Iridium (Ir,Os)		• (4)	
Pt-Fe alloy Pt_3Fe	• (1)	• (7)	
(Pt,Pd)-Fe alloy		• (8)	
Unnamed Pt(Fe,Cu,Ni)			• (5)
Irarsite IrAsS	• (199)	• (34)	• (11)
Hollingworthite RhAsS	• (11)	• (9)	
Platarsite PtAsS	• (26)	• (3)	
Ruarsite RuAsS	• (61)	• (3)	
Platarsite-ruarsite		• (19)	
Keithconnite $Pd_{20}Te_7$		• (3)	
Sperrylite $PtAs_2$	• (705)	• (4)	• (69)
Mayakite PdNiAs			• (1)
Geversite $PtSb_2$			• (1)
Stibiopalladinite Pd_5Sb_2	• (40)	• (1)	• (24)
Potarite PdHg	• (53)		
Mertieite-II $Pd_8(As,Sb)_3$	• (1)		• (1)
Unnamed Pd-As-Sb			• (6)
Unnamed Pd-Rh-As			• (1)
Unnamed Pd-Pt-Bi-Cu			• (1)
Ru-rich oxide (?)	• (4)		
Gold Au	• (1)		
Au-rich silver (Ag, Au)	• (5)		
Tetrauricupride AuCu			• (1)
Total number of PGM counted	1151	208	131

1 - PGM from highly altered podiform chromitite (Malitch et al. , 2001)

Geology and Sample Location

The Kraubath dunite-harzburgite massif, the largest dismembered mantle relict in the Eastern Alps, is situated within the Austrian Province of Styria. It have been interpreted as part of strongly deformed and metamorphosed ophiolite sequence, which forms part of the Speik Complex (Stumpfl and Ageed, 1981; Neubauer et al., 1989; Melcher, 2000). The prevalent chromitite type occurs as schlieren, deformed stringers and streaks of massive chromite not more than a few centimeters thick, considered as typical podiform chromitite. Sample K 142, which is from a small outcrop in the abandoned open pit chromite mine of Mitterberg, is representative of this type (Fig. 1). Another, less abundant type of chromitite (i.e. sheet-like orebodies, banded type) appears as layers and seams of densely disseminated euhedral to subhedral chromite in a stratigraphically higher level of the massif (Fig. 1). Sample K 134, typical of this chromitite type, is from a seam, 5-25 cm thick, which can be traced for more than 30 m along dip (30-60° to the north) (Fig. 1). Chemical composition of chromite varies from Cr# (100*Cr/(Cr+Al))=73-77 in the banded type to Cr#=81-86 in the podiform chromitite.

Analytical Techniques

Whole rock 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 platinum-group minerals (PGM) with associated minerals, both chromitite samples (K 134 and K 142) were first investigated in polished sections. Chromitite samples were, then, disintegrated by a method, which includes gradual milling followed by consequent removing and sieving of the two fine fractions (i.e. <37 µm and 37-90 µm). The heavy minerals (including PGM) of these two fractions were concentrated by a hydroseparation technique (Knauf, 1996) at NATI Research JSC, St. Petersburg, Russia, by reaching concentration factors between $4x10^4$ to $1x10^5$ times. Finally, each concentrate with PGM was mounted in epoxy blocks and polished in separate sections for further detailed microanalytical study. Microprobe analyses were carried out on an ARL-SEMQ microprobe with four wavelength-dispersive spectrometers and equipped with a LINK energy dispersive analyser at the Institute of Geological Sciences, University of Leoben (Austria).

PGE Concentrations in Whole Rock Samples

The total PGE concentrations in the two samples are relatively high (K 134: 833 ppb; K 142: 731 ppb), compared to typical ophiolitic chromitite. Banded chromitite (K 134) is characterised by enrichment of the less refractory PGE, such as Pd and Pt, over the more refractory PGE (IPGE-group:

Os, Ir, Ru), resulting in a positive slope in a chondrite-normalised PGE pattern (Fig. 2). It fits close to those of highly altered podiform chromitites from the mantle section and/or stratiform chromitites from the crustal section of ophiolites. On the contrary, the podiform chromitite (K 142) shows a negatively sloped PGE pattern (Fig. 2), similar to those characteristic of ophiolite-type podiform chromitites. The PGE pattern of podiform chromitite (K 142) matches well with the majority of negatively sloped PGE patterns of Kraubath chromite concentrates (Melcher, 2000).

PGE Mineralogy

Banded chromitite. A total of 13 different PGM and one Au-rich mineral was documented in banded chromitite (Table 1). Prior to the disintegration of the banded chromitite (sample K 134) Ru-, Pt- and Ir-rich minerals were observed as euhedral inclusions in polished sections (Fig. 3a, b). Euhedral laurite (RuS_2) in the size range of 3-15 µm predominates, followed by euhedral sperrylite ($PtAs_2$, up to 13.5 µm in diameter) and irarsite (IrAsS, up to 10 µm). PGE-poor sulfide is represented by pentlandite, which frequently forms single and rarely polyphase inclusions with laurite and irarsite (Fig. 3a). No PGM interstitial to chromite have been observed.

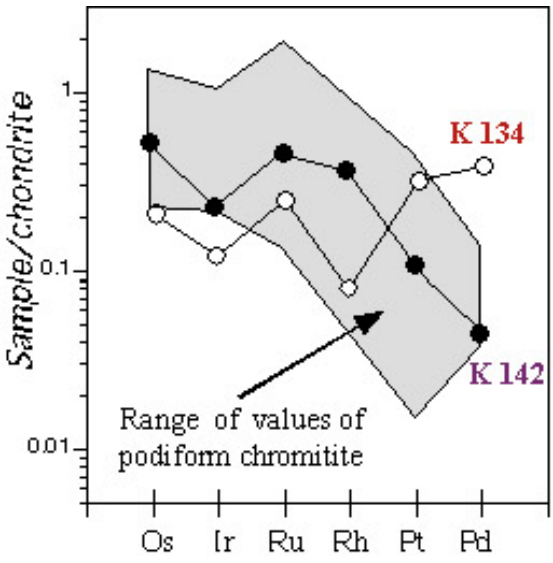

Figure 2. *Chondrite-normalised PGE patterns of banded (K 134) and podiform (K 142) chromitites from the Kraubath massif. Composition of chondrite according to McDonough and Sun (1995).*

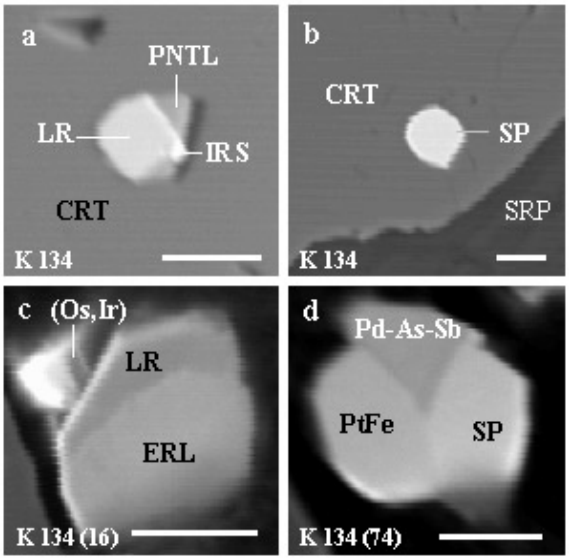

Figure 3. *Back scattered electron images of polyphase (a, c, d) and single (b) PGM inclusions in chromite from banded chromitite (sample K 134). LR - laurite, ERL - erlichmanite, (Os,Ir) - iridian osmium, IRS - irarsite, PNT - pentlandite, SP - sperrylite, PtFe - unnamed Pt-Fe(Cu,Ni) alloy, Pd-As-Sb - unnamed PGM, CRT - chromite, SRP - serpentine. Scale bar is 10 µm.*

Mineral concentrates of banded chromitite contains 99 PGM grains that comprise 78 monophase PGM and 21 polyphase PGM grains. The latter are commonly euhedral and display stable phase boundaries most frequently between two or three different Pt-, and Pd-rich minerals (Fig. 3d). PGM are dominated by sperrylite (53 %) and Pd antimonide (18 %), followed by Ir-sulfarsenide (9 %), Ru-Os sulfides (7 %), various Pd-As-Sb minerals (6 %) and unnamed Pt - base metal (BM) alloys (4 %) (Table 1). Most of them are found as both, single and polyphase grains. On the contrary unnamed Pt-BM alloys with a compositional range Pt(Fe,Ni,Cu)-Pt(Fe,Cu,Ni) are mainly restricted to polyphase grains (Fig. 3d). Rare PGM such as iridian osmium (Fig. 3c), As-mertieite II (?), Bi-geversite $Pt(Sb,Bi)_2$, mayakite (PdNiAs), unnamed Pd-Rh-As and Pt-Pd-Bi-Cu have been identified in polyphase inclusions consisting of at least 3 minerals. One inclusion of tetrauricupride AuCu in stibiopalladinite has been also observed.

Podiform chromitite. Twenty-one different PGM were identified among 89 single and 47 polyphase PGM grains of up to 100 micron in the podiform chromitite (Malitch et al., 2001; this study) resulting in a dominance of Ru-Os sulfides and various PGE sulfarsenides, followed by

compositionally different PGE-BM sulfides and Pt-Fe alloys (Table 1). PGE sulfides, PGE alloys and PGE sulfarsenides are considerably different from those observed in the banded type in terms of their composition and mineral associations (Table 1). For instance, PGE-sulfarsenides show complex, sometimes unconventional element substitutions, contrary to those in banded chromitite. They are mainly represented by irarsite and platarsite-ruarsite, followed by hollingworthite, while platarsite and ruarsite are less abundant.

Discussion and Conclusions

Detailed investigation of the PGM from the two distinct chromitites (banded and podiform types) of the Kraubath massif revealed high- to medium-temperature primary magmatic PGM assemblages. The high-temperature assemblage is dominated by laurite, which occurs in complex polyphase assemblages with alloys (Ir-Os, Os-Ir, Pt-Fe), sulfides (kashinite-bowieite, PGE-rich thiospinel series, braggite, unnamed (Ni,Fe,Cu)-(Ir,Rh)-S and Pd telluride (keithconnite). The medium-temperature assemblage is represented by sperrylite associated with unnamed Pt-BM alloy and Pd-rich minerals such as stibiopalladinite, mayakite, unnamed Pd-Rh-As and several other Pd-As-Sb minerals. The high-temperature assemblage is characteristic of podiform chromitite, while both assemblages are recorded in banded chromitite (Fig. 3). The latter is characterised by a wider range of conditions for PGM formation controlled by enhanced activities of S, As and Sb, while the podiform type is mainly constrained by variable sulfur fugacities. Therefore, our mineralogical evidence might be considered as an indication for the presence of Moho transition zone, showing signatures of both, the mantle and crustal sections of an ophiolite.

The occurrence of 29 different PGM and one gold-bearing mineral as observed from only two bedrock chromitite samples from the Kraubath massif is highly unusual for an ophiolitic environment. Such diversity of primary PGM assemblages containing all 6 PGE in both, laurite-dominated podiform chromitite as well as in uncommon sperrylite-dominated banded chromitite has been firstly observed in or close to the mantle section of an ophiolite. As a consequence, geologically, geochemically and mineralogically distinct banded chromitite from Kraubath might be considered as indicative rather for the transition zone of an ophiolite, closely above the mantle section with podiform chromitite, than as representative of the crustal cumulate pile.

Acknowledgements

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