

Solid inclusions in chrome-spinels and platinum group element concentrations from the Hochgrössen and Kraubath Ultramafic Massifs (Austria)

Their relationships to metamorphism and serpentinization

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Abstract. A great variety of platinum group mineral, sulfide and silicate inclusions in chrome spinel from Hochgrössen and Kraubath ultramafic massifs, and platinum group element contents of three different rock types have been investigated. Both ultramafic massifs are tectonically isolated bodies, variably serpentinized and metamorphosed (greenschist to lower amphibolite facies), and show ophiolitic geochemical affinities. The chromite from massive chromitites and disseminated in serpentinized dunites and serpentinites, exhibits compositional zonation as the result of alteration during serpentinization and metamorphism. Three distinctive alteration stages are indicated in the chrome-spinels from the Hochgrössen, whereas alteration is less significant in chromites from Kraubath: The core of chrome spinel represents the least altered part, surrounded by an inner rim characterized by slight compositional differences in Cr, Mn, Fe^{2+} and Al with respect to the core. The outer rim is formed by ferritchromite with a sharp boundary to the inner rim and shows a significant decrease of Al, Mg, Cr and increase of Fe^{2+} , Fe^{3+} and Ni compared to the core. Two different groups of inclusions in chrome-spinel are present: the first group occurs within the chromite core, and comprises olivine, orthopyroxene, amphibole, sulfides and platinum-group minerals, i.e. dominated by Ru–Os–Ir-sulfides. The second group is formed by chlorite, serpentine, galena, pyrite, arsenopyrite, Pt–Pd–Rh-dominated sulfarsenides and sperrylite. In particular the abundance of Pt–Pd–Rh-sulfarsenides and arsenides is typical of both ultramafic massifs and is very unusual for chromitites from ophiolites. Morphology, paragenesis and chemical composition indicate a different origin for these two groups of inclusions. The first group is intimately related to the crystallisation of the chromite host. The second group of inclusions clearly displays a secondary formation during ser-

pentinization and metamorphism, closely related to the alteration of chrome-spinel and the development of ferritchromite. The distribution patterns of the platinum group elements from massive chromitites, disseminated chrome-spinel bearing serpentinites and serpentinites exhibit variable enrichment of Rh, Pt and Pd, Rh, Pt for the Hochgrössen and Kraubath massifs, respectively. These results are in accordance with the occurrence and distribution of platinum-group mineral phases. A remobilisation of Pt, Pd and Rh, together with Ni, Cu and possibly Fe as bisulfide and/or hydroxide complexes and deposition of metals by the reaction of the metal bearing hydrothermal fluid with chromite is proposed.

1 Introduction

Over the past few years an increasing amount of data on mineral inclusions in chrome-spinel from various tectonic settings such as ophiolites, volcanic sills and stratiform complexes has become available (Talkington et al. 1984; Prichard et al. 1987; Lorand and Cottin 1987). Inclusions of silicates (olivine, pyroxene, amphibole and mica), Fe–Ni–Cu sulfides and platinum group minerals (dominated by Ru–Ir–Os-rich sulfides and alloys) are common in podiform chromite ores from mantle sequences of ophiolites (Talkington et al. 1984; Prichard et al. 1987; Lorand and Ceuleneer 1989). However, the origin of the mineral inclusions in chromite is still controversial. Several different models in terms of timing and mode of entrapment of these inclusions with respect to the precipitation of the chrome-spinel have been postulated (Talkington et al. 1984; Auge 1987; Hulbert and Gruenewaldt 1985; Lorand and Cottin 1987; Lorand and Cottin 1989).

The Hochgrössen and Kraubath ultramafic massifs representing two strongly serpentinized and metamorphosed dismembered relics of an early Palaeozoic ophiolite complex (El Aageed et al. 1980), provide an excellent

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Table 1. Selected electron-microprobe analyses of silicate and sulfide inclusions and corresponding groundmass phases from the Hochgrößen (HG) and Kraubath (KR) ultramafic massifs. Further analytical data are available from the authors on request

wt%	Ol-incl. (HG)	Ol close to chromite (HG)	matrix-Ol (HG) ^a	matrix-Ol (KR)	Opx-incl (HG)	Amph- incl (HG)	matrix-Serp close to chromite (HG)
SiO ₂	42.148	41.184	43.02	39.924	56.092	50.312	38.486
TiO ₂	nd	nd	nd	nd	0.048	0.105	0.088
Al ₂ O ₃	nd	nd	nd	nd	0.264	5.044	3.287
FeO	2.716	2.632	2.71	11.482	6.268	2.280	3.289
MnO	0.055	0.263	0.25	0.204	0.196	0.166	0.000
NiO	0.412	0.131	0.07	0.044	0.059	0.018	0.085
Cr ₂ O ₃	nd	nd	nd	nd	0.161	0.494	2.398
MgO	55.017	54.837	52.50	47.548	34.858	22.016	37.545
CaO	nd	nd	nd	nd	0.289	12.623	0.073
Na ₂ O	nd	nd	nd	nd	0.000	2.031	0.099
K ₂ O	nd	nd	nd	nd	0.000	0.258	0.133
Total	100.348	99.046	98.55	99.201	98.236	95.348	85.484
Fo%	97.3	97.7	95.0	88.1	En % 90.9	cations per 23	14 oxygens
					Si	7.176	3.721
					Al ^{IV}	0.824	0.279
					Al ^{VI}	0.024	0.096
					Ti	0.011	0.008
					Fe ²	0.038	0.266
					F ³	0.292	Cr 0.183
					Mn	0.020	Ni 0.007
					Mg	4.682	5.411
					Ca	1.929	0.008
					Na	0.562	0.019
					K	0.047	0.016
					Mg#	1.006	Cl wt% 0.585
Sulfides							
	Pentlandite-incl.		matrix-Pentlandites		Millerite (?)		
wt%	(HG)	(KR)	(HG)	(KR)	(HG)		
S	34.736	33.763	34.305	33.842	36.731		
Fe	23.432	28.278	29.429	35.463	9.439		
Cu	0.000	0.000	0.000	2.962	0.000		
Co	0.292	1.652	2.337	2.241	0.005		
Ni	41.674	36.093	33.713	24.514	53.856		
Pd	0.075	0.008	0.002	0.002	0.473		
Total	100.209	99.795	99.787	99.024	100.498		
at%							
S	48.834	47.817	48.395	48.084	51.225		
Fe	18.914	22.994	23.836	28.969	7.557		
Cu	0.000	0.000	0.000	2.144	0.000		
Co	0.223	1.273	1.794	1.734	traces		
Ni	31.997	27.917	25.975	19.069	41.019		
Pd	0.032	traces	—	—	0.199		

^a Analysis from El Ageed (1979)

Table 2. Occurrence and distribution of sulfide and PGM inclusions compared with those occurring interstitially with silicates from the Hochgrössen (HG) and Kraubath (KR) ultramafic massif

Sulfides	inclusions in chromite core		inclusions in ferrit-chromite		interstitially with silicates	
	(HG)	(KR)	(HG)	(KR)	(HG)	(KR)
	Pentlandite (Ni, Fe) ₉ S ₈	25	20	4	—	abundant
Chalcopyrite CuFeS ₂	10	6	4	—	abundant	
Heazlewoodite Ni ₃ S ₂	15	7	2	—	rare	
Pyrrite FeS ₂	2	2	—	2	rare	
Galena PbS	—	—	10	4	—	
Arsenopyrite FeAsS	—	—	2	4	rare	
Millerite (?) NiS	1	—	—	—	—	
PGM						
Laurite RuS ₂	40	15	12	—	—	
Erlichmanite (?) OsS ₂	1	—	1	—	—	
Cooperite PtS	—	—	3	—	—	
Irarsite IrAsS	7	—	14	—	5	—
Hollingworthite RhAsS	—	—	5	—	5	—
Platarsite PtAsS	1	—	3	—	2	—
Mixed Sulf-arsenides Sperryllite	3	—	18	—	8	5
Pt—Cu—Sulf-arsenide	4	—	23	—	24	6
Pd—Pt—Sb-alloy	1	—	—	—	—	—
Pt-alloy	3	—	—	—	1	—
	2	—	—	—	—	—

opportunity for the study of mineral inclusions in chrome-spinel, the preliminary results of which have been reported by Thalhammer and Stumpfl (1988):

(1) There is a great variety of solid inclusions, in particular platinum group minerals, in the almost unaltered chromite. They are comparable with those from podiform chromite ores elsewhere.

(2) Serpentinization and metamorphism have also considerably affected the chromite resulting in alteration and formation of ferritchromite rims. These alteration rims host a remarkable amount of mineral inclusions, different in type and distribution, and unusual for ophiolitic chromitites. Their characteristics suggest a close relationship to the alteration of chromite during serpentin-

Table 3. PGE and Au contents of massive chromitites (analyses 1–4), disseminated chrome-spinel containing serpentinites (analysis 5) and serpentinites (analyses 6–8) from the Hochgrössen (HG) and Kraubath (KR) ultramafic massifs. Abundances in ppb

Concentrations in ppb	1	2	3	4	5	6	7	8
	HG6	HG5	HGE	K10	HG8	HG92	K100	K2
Os	250	10	67	34	2	3	1	6
Ir	310	7.9	130	52	1.3	2.9	1.7	5.2
Ru	620	50	190	120	10	3	5	17
Rh	120	5	130	98	4	2	6	15
Pt	940	8	390	470	13	34	22	56
Pd	29	4	33	390	3	3	150	190
Au	14	2	3	2	3	6	4	4
Pt/Pt+Pd	0.67	0.92	0.81	0.55	0.81	0.92	0.13	0.23
Ir/Pt	0.33	0.99	0.33	0.11	0.10	0.09	0.08	0.09

ization and metamorphism, as assumed by Thalhammer and Stumpfl (1988).

This paper focuses in particular on the alteration history of the chrome-spinel and the occurrence of silicate, sulfide and platinum-group mineral inclusions in the ferritchromite rim. We also present whole rock platinum group element abundances from chromitites, chrome-spinel-bearing serpentinites and serpentinites in order to correlate these data with the results from the platinum group mineral inclusions. Finally, we discuss the possible formation of platinum group minerals and sulfides in the course of remobilization, fluid-transport and precipitation of metals during the processes of serpentinization and metamorphism.

II Techniques

PGM (platinum group minerals) and other solid inclusions were studied in polished block and thin sections. Precise polishing has been carried out on a Rehwald polishing machine.

For quantitative and semi-quantitative mineral analyses, an ARL-SEMQ electron microprobe, equipped with a Link Systems energy-dispersive (EDS) 860 analyser, series 2, was used under the same operating conditions described in Thalhammer and Stumpfl (1988). Corrections were performed according to the Magic IV program and to Bence and Albee (1968). Calibration was achieved using 40 international mineral and single element standards.

Low concentration of Fe and Cr apparent in the microprobe analyses (Tables 1 and 3) of platinum group mineral phases <6 µm in diameter are ascribed to radiation from the associated chromite. Atomic proportions were calculated after subtraction of Fe and Cr and recalculated to 100%.

Many PGM inclusions exhibit compositional zonation or form composite grains of different minute PGM phases. Back-scattered electron images have been studied using a Leitz AMR 1000, in order to identify the surface outline of the compositional differences of these PGM phases. Background scatter in single-element scans were deleted by photographic techniques to facilitate better recognition of mineral shapes and phase boundaries.

The concentration of PGE and Au in nine representative samples have been determined by fire assay neutron activation analyses, by Neutron Activation Services, Ltd., Hamilton, Canada, following the method of Hoffmann et al. (1978). These samples comprise schlieren-type chromitites, disseminated chromite-bearing ser-

Table 4. Selected electron-microprobe analyses of platinum group minerals from the Hochgrössen (HG) and Kraubath (KR) ultramafic massifs. Atomic proportions (at%) calculated after subtraction of Fe and Cr. Further analytical data are available from the authors on request. 1–2, PGM inclusions within chromite core; 3, PGM inclusion in ferritchromite rim; 4, PGM inclusion (composition close to OsS₂) situated in inner chromite rim (stage B); 5, irarsite inclusion within chromite core; 6, irarsite inclusion in ferritchromite rim; 7–9, zonation of irarsite inclusion at the edge of chromite core; 10, platarsite type-1 inclusion in ferritchromite rim, similar to platarsite from Onverwacht, Transvaal (Cabri et al. 1977); 11, platarsite of type 2, inclusion within chromite core; 12, PGM alloy forming part of a sulfide inclusion in chromite core

wt%	Sulfides						Sulfarsenides					
	1 (KR)	2 (HG)	3 (HG)	4 (HG)	5 (HG)	6 (HG)	7 (HG) core	8 (HG)	9 (HG) rim	10 (HG)	11 (HG)	12 (HG)
Os	3.672	6.622	27.228	42.966	0.000	3.135	4.481	8.993	14.958	2.822	12.007	4.776
Ir	2.585	3.684	5.639	11.493	48.325	32.701	43.486	36.539	17.911	8.054	6.863	2.135
Ru	49.596	47.342	30.632	4.854	0.990	0.198	0.059	0.896	1.997	5.453	4.596	0.684
Rh	2.045	2.943	1.676	3.147	5.907	6.005	6.000	5.760	5.259	11.842	2.097	1.459
Pt	0.582	0.033	0.000	10.822	4.244	15.391	4.074	6.617	16.958	29.455	30.488	70.883
Pd	1.998	1.851	1.231	0.814	0.002	0.004	1.964	3.902	2.098	1.089	1.231	4.965
As	2.999	2.737	1.537	5.954	25.821	27.537	25.241	23.221	25.668	27.078	28.319	0.887
S	34.177	35.086	30.514	20.880	11.881	11.922	11.525	11.662	11.639	11.438	12.100	0.120
Fe	2.166	0.064	1.687	nd	0.874	2.655	2.442	1.866	3.124	1.804	1.705	8.683
Cr	0.268	0.000	0.000	nd	1.108	nd	nd	nd	nd	nd	nd	nd
Total	100.088	100.353	100.144	100.930	99.152	99.548	99.272	99.455	99.612	99.035	99.406	94.592

at%	1 (KR)	2 (HG)	3 (HG)	4 (HG)	5 (HG)	6 (HG)	7 (HG) core	8 (HG)	9 (HG) rim	10 (HG)	11 (HG)	12 (HG)
Os	1.137	2.060	9.688	19.516	0.000	1.502	2.300	4.489	7.481	1.357	5.796	5.176
Ir	0.778	1.118	1.965	5.181	23.769	15.962	21.656	18.147	8.807	3.801	3.312	2.277
Ru	29.384	27.543	20.528	4.145	0.947	0.188	0.057	0.860	1.894	4.887	4.140	1.449
Rh	1.197	1.707	1.084	2.677	5.398	5.446	5.558	5.349	4.830	10.407	1.840	2.899
Pt	0.179	0.012	0.000	4.750	2.083	7.418	2.012	3.247	8.239	13.665	14.352	75.156
Pd	1.137	1.000	0.813	0.691	traces	traces	1.725	3.534	1.894	0.905	1.104	9.731
As	2.394	2.177	1.423	6.822	32.670	34.554	32.292	29.608	32.481	32.670	34.774	2.484
S	63.794	64.383	64.499	56.218	35.133	34.930	34.400	34.766	34.374	32.308	34.682	0.828

pentinite and serpentinite with accessory chrome-spinels from both areas (analytical data are summarized in Table 3). For normalization (the normalized patterns are illustrated in Fig. 6) the C1 chondrite values of Barnes et al. (1985) have been used.

III Regional geology of the Hochgrössen and Kraubath ultramafic massifs

The ultramafic massifs of the Hochgrössen and Kraubath are situated within the Austrian province of Styria (Niedere Tauern). This part of the Eastern Alps belongs to the Middle Austro Alpine Unit, characterized mainly by thick volcano-sedimentary sequences enveloping metagranites and gneisses (Fig. 1).

The Middle Austro Alpine complex of the areas studied is divided into the Muriden, Koriden and Micaschist units. The ultramafic massifs of the Hochgrössen and Kraubath are part of the Speik Complex of the Muriden unit. This Speik Complex comprises a basal ophiolitic suture, possibly of Ordovician/Silurian age (Frisch et al. 1984), and a sequence of banded amphibolites of Cambrian age. The ophiolitic nature of these ultramafic bodies has been demonstrated from their geochemistry and the composition of the chromites (El Ageed 1979; Haditsch et al. 1981).

Both the Hochgrössen and the Kraubath ultramafic massifs are rootless and have tectonic contacts with the country rock. The ultramafic rocks of Kraubath comprise mainly dunites, harzburgites and bronzitites. According to previous workers, the rocks

are classified as belonging to a metamorphic harzburgite series representing heavily depleted residual mantle material of an ancient ophiolite sequence (El Ageed 1979; El Ageed et al. 1980; Haditsch et al. 1981). Serpentinization is widespread, and its intensity is related to regional tectonic features. Autometasomatism and ingress of epigenetic CO₂-rich fluids resulted in local formation of talc pseudomorphs after enstatite and magnesite (Haditsch et al. 1982).

The Hochgrössen complex consists predominantly of dunites with subordinate intercalations of pyroxenites. They are interpreted as representing the ultramafic cumulate sequence in the postulated ophiolite suite (El Ageed 1979). The degree of serpentinization is very heterogeneous and, as at Kraubath, related to tectonic structures. In faults and at the outer rim of the ultramafic body, talc-carbonate rocks have been produced by CO₂ metasomatism.

IV The chrome-spinels from the Hochgrössen and Kraubath ultramafic massifs

In the Hochgrössen and Kraubath ultramafic massifs, chrome-spinels occur as schlieren-type concentrates (so called chromitites containing more than 70% chrome-spinel) and as disseminations in both serpentinites and serpentinized dunites. The shape, occurrence and grain size of chrome-spinels, as well as the texture and distribution of the chromitites have been described in detail by El Ageed (1979), El Ageed et al. (1980) and Thalhammer and Stumpfl (1988).

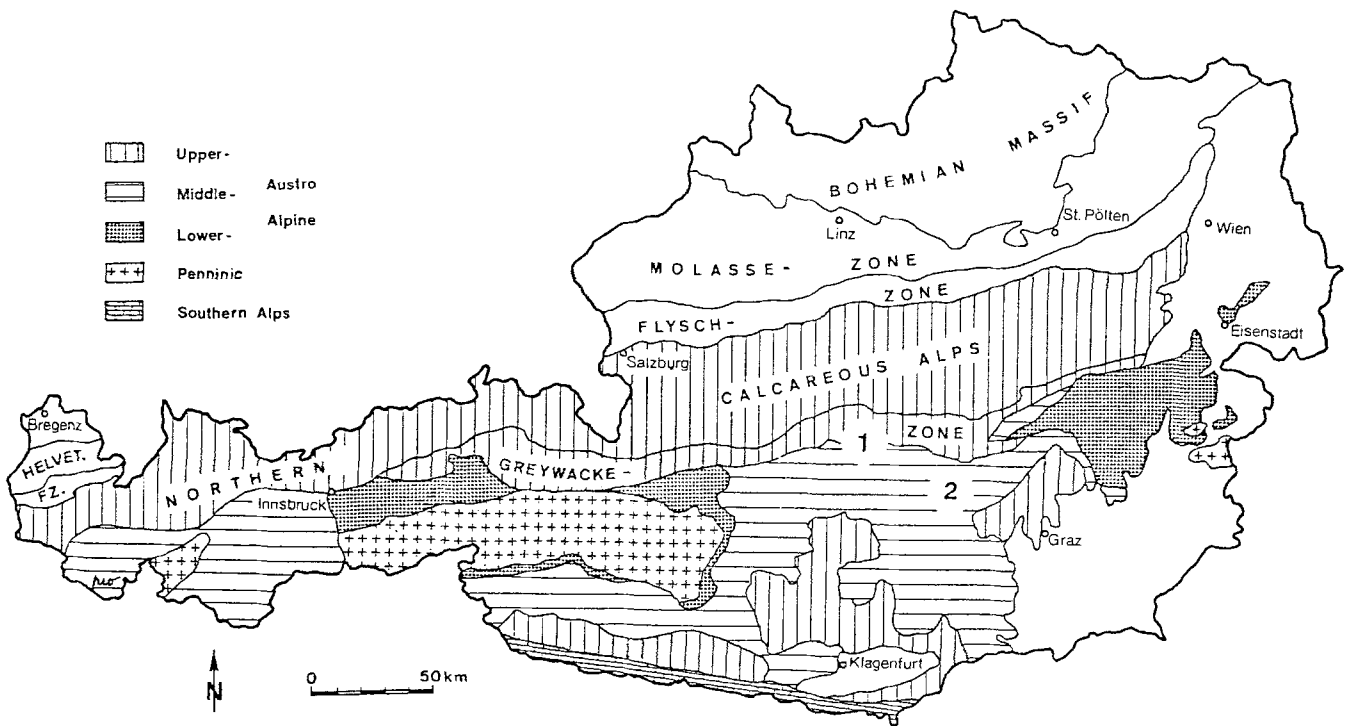


Fig. 1. Geological sketch map of Austria showing the major tectonic units of the Eastern Alps. 1, location of the Hochgrössen massif; 2, location of the Kraubath massif

Chemistry of chromites

In the Hochgrössen massif the majority of chrome-spinels in schlieren-type chromitites and almost all disseminated chromites show zonation defined by optical and compositional differences, whereas zoning of chrome-spinels from the Kraubath ultramafic body occurs only rarely. Mineralogical and chemical zoning has been reported in numerous studies (Spangenburg 1943; Beeson and Jackson 1969; Evans and Frost 1975; Bliss and McLean 1975; Wylie et al. 1987 and others, cited in Wylie et al. 1987); therefore, only the most important characteristics of chrome-spinel zonation, i.e. stages A–C, are summarized in the following. The chemical compositions of all analysed chromites with respect to Fe^{3+} , Cr and Al are illustrated in Fig. 2.

Stage A

The cores of chromite grains are anhedral, irregularly shaped and homogeneous with respect to chemical composition and optical properties. In the chrome-spinels from Kraubath, the core forms the predominant part of the grain.

The chromite cores from both the Hochgrössen and Kraubath ultramafic massifs are Cr-rich, metallurgical grade chromitites (Fig. 2), with relatively low Al_2O_3 in the range of 5 to 13 wt%. Mg/Fe^{2+} ratios are in the range 0.8 to 1.5 in Hochgrössen chrome-spinels, whereas

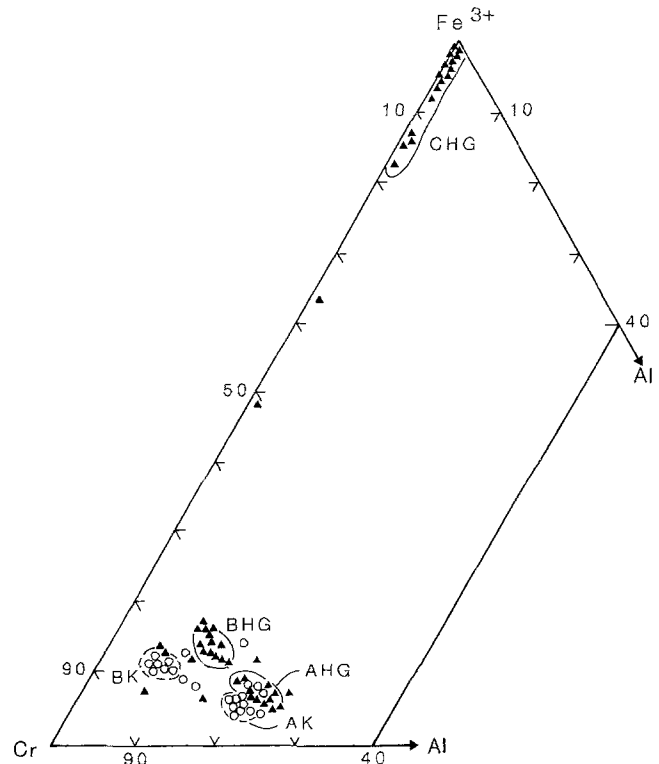


Fig. 2. Compositional zonation of chrome-spinels from the Hochgrössen (filled triangles) and Kraubath ultramafic massifs (open circles), illustrated in the Fe^{3+} –Cr–Al triangle. HG, Hochgrössen; K, Kraubath; A, B, C refer to zonation stages (see text)

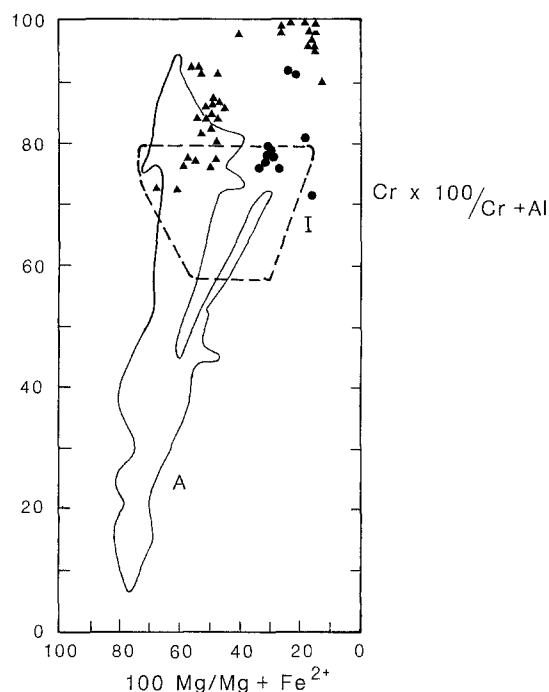


Fig. 3. Composition of chrome-spinels in the $\text{Cr}/\text{Cr}+\text{Al}$ vs $\text{Mg}/\text{Mg}+\text{Fe}^{2+}$ diagram. Defined fields for alpine-type chromites (*A*) and that for stratiform intrusions (*I*) (after Irvine 1967; Dick and Bullen 1984) are for comparison. Symbols: *Filled triangles*, chrome-spinels from the Hochgrössen; *filled circles*, chrome-spinels from Kraubath

the Kraubath chromites have distinctly lower ratios of 0.2–0.5, as shown in the $100 \text{ Cr}/(\text{Cr}+\text{Al})$ vs $100 \text{ Mg}/(\text{Mg}+\text{Fe}^{2+})$ plot (Fig. 3). This difference, i.e. in X_{mg} ($X_{\text{mg}} = 100 \text{ Mg}/[\text{Mg}+\text{Fe}^{2+}]$), is coupled with a slight variation in the NiO content. Chromites from Hochgrössen show NiO values up to 0.13 wt% in contrast to those from the Kraubath massif which are generally lower. TiO_2 contents are in the range of 0.2–0.8 wt% for chromites from both massifs. In the Mg/Fe^{2+} against TiO_2 diagram both massifs show a tendency to a negative correlation between the Mg/Fe^{2+} ratio and TiO_2 (Fig. 4).

Stage B

is represented by a slightly higher reflecting rim surrounding the core. Numerous inclusions (mainly serpentine phases, Fig. 5a), and slight increase in Cr, Mn and Fe^{2+} and decrease in Al compared to the core are characteristic (Fig. 2). The changes in chemical composition do not exceed 5 wt%.

Stage C

forms the outer rim of chrome-spinel grains with a sharp boundary to stage B (Fig. 5a). The chemical composition is characterised by a considerable loss in Al, Mg and Cr contents corresponding with great increases in Fe^{2+} , Fe^{3+} and Ni (Figs. 2 and 3). Within this zone, referred to as ferritchromite, composition changes grad-

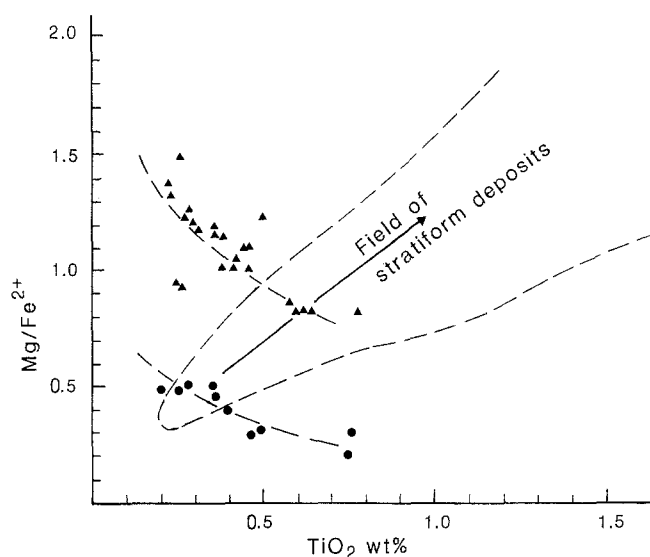


Fig. 4. Mg/Fe^{2+} vs TiO_2 variation of chrome-spinels from the Hochgrössen (*filled triangles*) and Kraubath massif (*filled circles*). Arrow indicates the general trend for chromites in stratiform deposits (Dickey 1975)

ually. The final product of this chemical transformation, appearing at the margin of this zone, is a Cr-bearing magnetite. Stage C is only present in chromites from the Hochgrössen massif.

V Sulfide and silicate inclusions in chrome-spinels

Silicate inclusions

Olivine, orthopyroxene, amphibole, chlorite and serpentine have been identified as inclusions in chromites from the Hochgrössen and Kraubath massifs. Olivine, orthopyroxene and amphibole inclusions have only been found in Hochgrössen chromites, and there exclusively in massive chromitites within the chromite core. Occasionally their distribution displays a tendency to concentrate along the peripheral zone of the chrome-spinel mimicking the shape of the core (Fig. 5a). Chlorite and serpentine inclusions are quite common from both massifs, either randomly distributed or showing a preference for the ferritchromite rim.

Olivine shows anhedral, rounded crystal shapes (Fig. 5c) and a grain size in the range of 30–120 μm . Quite commonly olivine inclusions are rimmed by serpentine and/or chlorite and are rarely cross-cut by chlorite laths. Their chemical composition (Table 1) is characterized by high Ni (in the range of 0.17 to 0.44 wt% NiO) and Mg contents ($\text{Fo}=97.2$ to 98.1). They are distinctive from cumulus olivines which exhibit lower Ni and Mg contents ($\text{Fo}=90$ to 94; Table 1).

Orthopyroxene exhibits subhedral to anhedral crystal shapes, or occurs as laths. Grain size varies between 60 and 120 μm . Microprobe analyses showed an En content of 90–91 (Table 1).

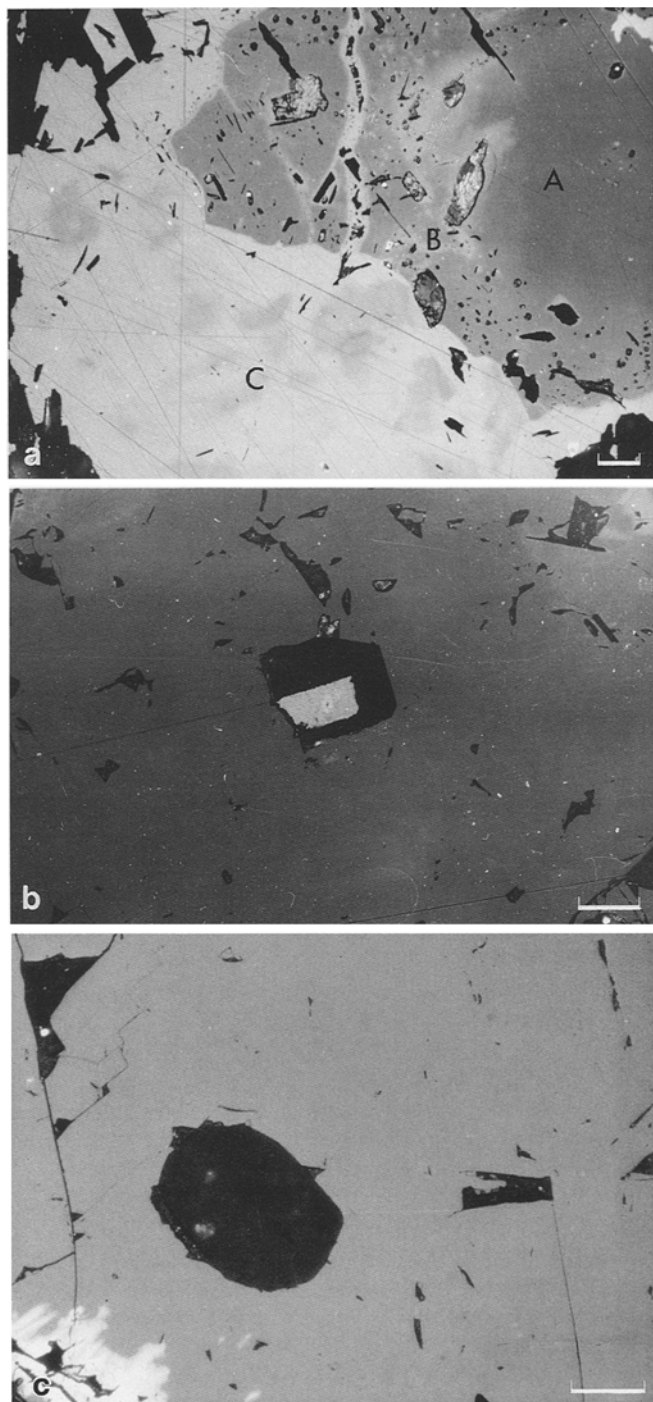


Fig. 5. a Alteration of chrome-spinel showing chrome-spinel core (A), and alteration stages B (B) and C (C). Note the occurrence of numerous inclusions in particular within alteration stage B and also in C. Block-, needle- and lath-shaped inclusions are serpentine. Reflected-light, oil immersion, parallel nicols; scale bar refers to 25 μ . b Amphibole-chlorite inclusion within chromite core. Dark phase represents amphibole, lath-shaped phase is chlorite. Reflected-light, oil immersion, parallel nicols; scale bar refers to 60 μ . c Rounded olivine inclusion within homogeneous chrome-spinel. Reflected light, oil immersion; scale bar refers to 45 μ .

The compositional characteristics of both olivine and orthopyroxene inclusions are in good agreement with earlier data by Talkington et al. (1984), Auge (1987) and Lorand and Ceuleneer (1989).

Amphibole inclusions are mainly subhedral with a diameter of 25–40 μ m and seem to be locally concentrated in the Hochgrössen chromitites (Fig. 5b). They have been found abundantly in two specimens and nowhere else. Amphibole inclusions are rarely surrounded by a thick rim of ferritchromite indicating a reaction zone formed during serpentinization and metamorphism. Microprobe analyses reveal almost Ti-free alkali amphiboles with Na₂O contents up to 2.1 wt% and Cr contents up to 0.3 wt% Cr₂O₃ (Table 1). They differ significantly from Ti-rich pargasite and/or kaersutite in unaltered chromite from Oman (Lorand and Ceuleneer 1989).

Chlorite occurs as a lath-shaped, patchy or blocky phase, in most cases associated with or cross-cutting olivine or amphibole inclusions (Fig. 5b). Occasionally, it surrounds olivine inclusions. Mg-chlorite is characterized by high Cr₂O₃ contents, which range up to 3.8 wt%. No differences exist between Mg-chlorite inclusions and matrix chlorites. Chlorite inclusions from the Kraubath massif exhibit slightly higher Fe contents than those from the Hochgrössen.

Serpentine has been identified either associated with chlorite cross-cutting or surrounding olivine inclusions, or as lath-shaped inclusions in ferritchromite (Fig. 5a). Microprobe analyses revealed identical chemical composition of serpentine inclusions and matrix serpentines. Moreover, serpentine from the Hochgrössen shows distinctly lower Fe contents than that from Kraubath in both inclusion and matrix serpentines. Cr and Ni in serpentine from both massifs vary and can reach 2.4 wt% Cr₂O₃ and 0.5 wt% NiO, respectively. Some serpentines close to interstitial sulfides and/or PGM, or bordering altered chromite contain up to 0.6 wt% Cl (Table 1).

The observations stressed above, i.e. occurrence of olivine, orthopyroxene and amphibole inclusions (first order silicate inclusions) within chromite cores, their crystal shape and abundant smooth contacts with the chromite host, strongly suggest that they have originated prior to overprint of metamorphism and are intimately related to the formation of the host chromite.

Chlorite and serpentine inclusions are secondary and formed as a result of serpentinization and metamorphism. The compositional differences between inclusions from the Hochgrössen massif and those from Kraubath can be attributed to host rock compositional differences. They are consistent with differences between cumulus olivine and chromite from the Hochgrössen and Kraubath, respectively (El Ageed 1979; this study).

Sulfide inclusions

By far the most abundant sulfide inclusion is pentlandite followed by heazlewoodite, chalcopyrite and pyrite. Ar-

senopyrite, galena and a Fe-rich Ni-sulfide, possibly millerite, occur only very rarely. The type and occurrence of sulfide inclusions is listed in Table 2. The majority are one-phase inclusions. In places, two-phase inclusions of pentlandite-galena, pentlandite-heazlewoodite and pentlandite-serpentine have been observed.

Pentlandite shows variable grain size (3–25 μm in diameter) and crystal shape (euhedral-anhedral) and occurs mainly in homogeneous chromite cores. In places, inclusions in ferritchromite can be observed. They occur in both schlieren-type chromitites and disseminated Cr-spinel grains with no preference. The majority exhibit random distribution. However, in places small pentlandite inclusions (2–5 μm) within chromite core show trail-like alignment, cross-cutting the grain boundaries of chromite without marked change in the direction of their trail, indicating secondary origin (Roedder 1981). The small grain-size of the latter prevented quantitative electron microprobe analyses.

Microprobe analyses reveal Co-poor, Ni-rich compositions with Fe/Ni ratios in the range of 0.88 to 0.58 from both massifs. The Fe content of pentlandites from the Kraubath massif is slightly higher than that from the Hochgrössen (Table 1). Pentlandite occurring interstitially with silicates shows distinctly lower Ni and higher Fe and Co contents (Fe/Ni ratios lie in the range of 1.2 to 0.8), as compared to pentlandite inclusions. Again interstitial pentlandites from Kraubath are richer in Fe and additionally exhibit higher Cu contents (up to 5.0 wt%) than those from the Hochgrössen massif.

One Fe-rich Ni-sulfide inclusion has been found in chromite from Hochgrössen. The chemical composition, illustrated in Table 1, is similar to millerite.

Chalcopyrite, *heazlewoodite*, *arsenopyrite* and *galena* inclusions are rare. The majority of these phases are very small (<4 μm in diameter) and have therefore been identified only qualitatively. Chalcopyrite and heazlewoodite inclusions occur preferentially in chromite cores, mainly of subhedral to anhedral crystal shape, whereas galena, arsenopyrite and pyrite inclusions have been found exclusively in altered chromite rims.

Two fundamentally different groups of silicate and sulfide inclusions in chromites from Hochgrössen and Kraubath are present: (1) Inclusions within homogeneous chromite cores, comprising sulfides, olivine, orthopyroxene and amphibole. The sulfides forming discrete inclusions, are characterized by high Ni contents and are thus clearly distinctive from their interstitial counterparts (Table 1). The silicates are Mg-, Ni- and alkali-rich, and there are indications of compositional differences between the inclusions and equivalent interstitial phases, e.g. olivine (Table 1). These results are in good agreement with earlier data of Stockman and Hlava (1984), Talkington et al. (1984), Prichard et al. (1987) and Lorand and Ceuleneer (1989), showing a close relationship to the formation of chrome-spinel. (2) Serpentine, chlorite and sulfides such as galena, arsenopyrite and chalcopyrite occurring in ferritchromite (Table 2) often exhibit a relationship to fractures and fissures of

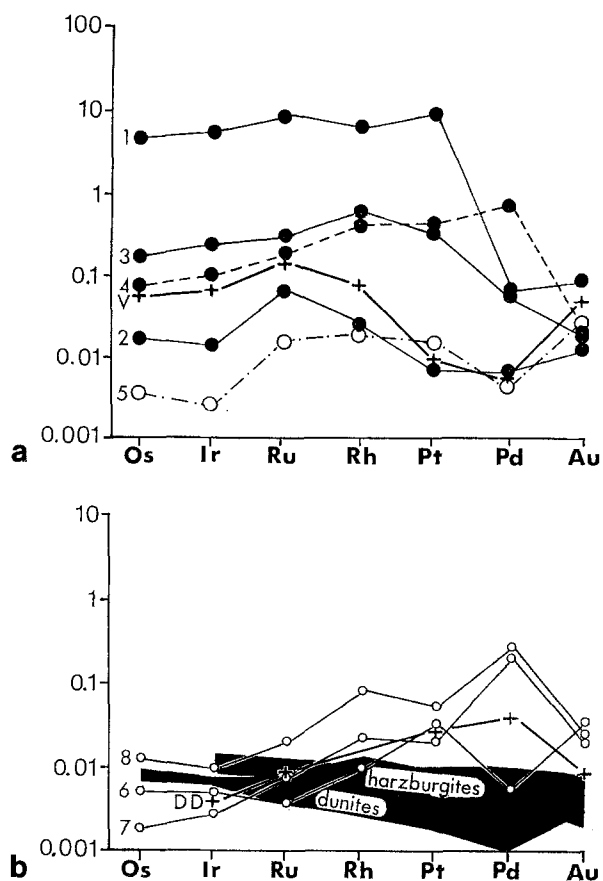


Fig. 6a, b. Chondrite normalized (normalizing values after Barnes et al. 1985) distribution patterns of PGE from the Hochgrössen and Kraubath massifs. **a** PGE patterns of massive chromitites from the Hochgrössen (1–3) and from Kraubath (4), as well as from a disseminated chrome-spinel bearing serpentinite from the Hochgrössen (5). A PGE distribution pattern typical for chromitites of ophiolites (V, Vourinos, Economou 1986) is shown for comparison. Symbols: Filled circles, massive chromitites; open circles, disseminated chrome-spinel bearing serpentinite; crosses, chromitite from Vourinos, Greece. **b** PGE patterns of serpentinites from the Hochgrössen (6) and Kraubath (7, 8). Patterns of dunites, harzburgites and a highly differentiated dunite from a cumulate sequence (DD, cross symbols) are for comparison. Data were taken from Barnes et al. (1985)

their host; occasionally, chlorite and/or serpentine show a tendency to form rims on and cross-cutting laths in olivine and/or amphibole inclusions within chrome-spinel cores (Fig. 5b). The chemical composition of both silicate and sulfide inclusions is not distinctive from the corresponding groundmass phases.

VI Distribution of platinum-group elements (PGE)

(a) PGE in schlieren-type chromitites

The overall abundance of PGE in chromitites from both massifs is about 0.3 times chondritic. One pattern (HG5, analysis 2 in Fig. 6a) from the Hochgrössen with the lowest PGE concentrations shows an increasing slope from Os to Ru and a decrease from Ru to Pd, reflecting a significant enrichment of IPGE (IPGE = Os, Ir and Ru) relative to PPGE (PPGE = Rh, Pt and Pd), ex-

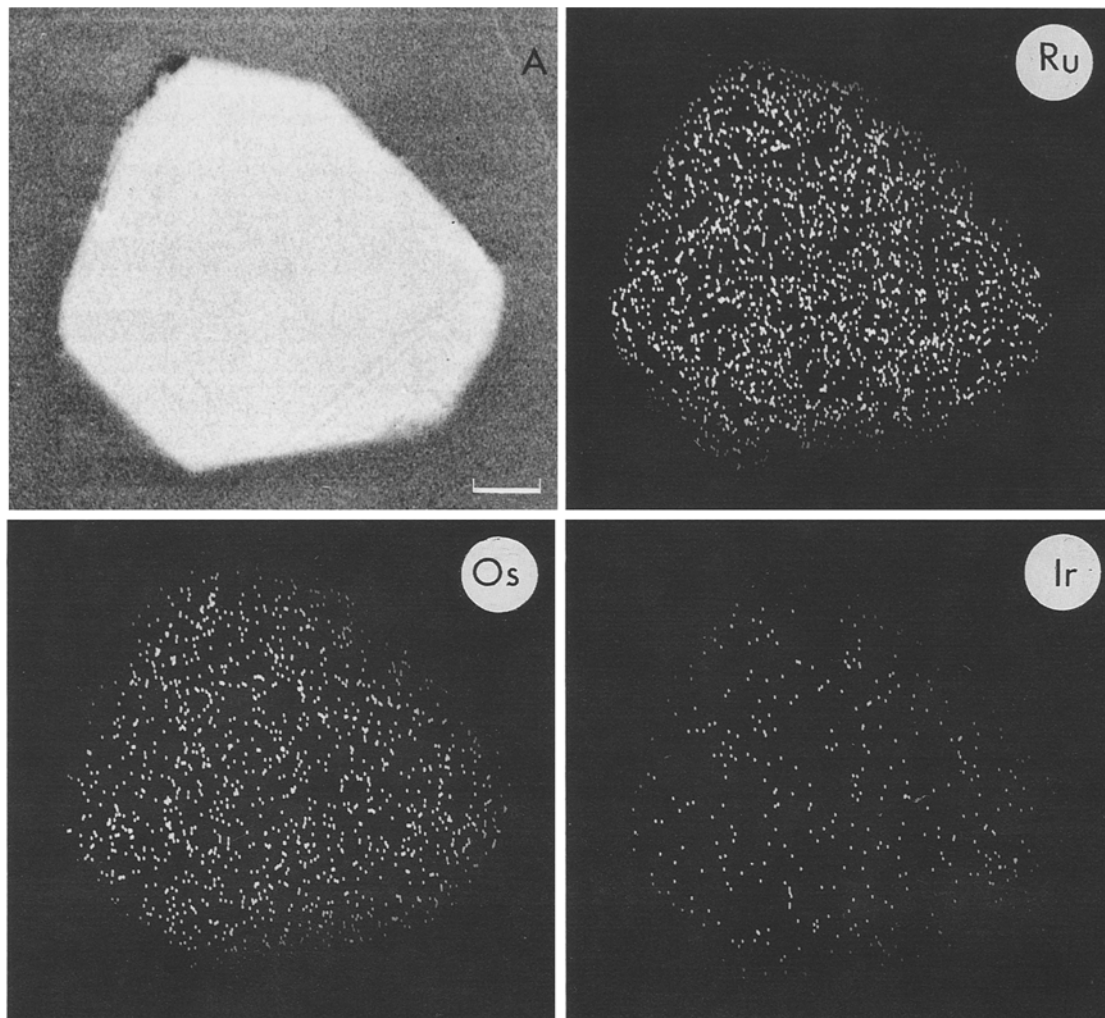


Fig. 7. Reflected-light photomicrograph (A) of an euhedral laurite inclusion within chrome-spinel core, and single-element scans for Ru, Os and Ir. Note that the three PGE do not show any zonation. Scale bar refers to 2 μ

pressed also by the Ir/Pt ratio of 0.99 (Table 3). This pattern is typical for ophiolitic chromitites from various localities and distinctive from most other mafic and ultramafic rock sequences (Page et al. 1984; Economou 1986; Talkington and Watkinson 1986).

However, the other patterns illustrated in Fig. 6a exhibit generally higher abundances of PGE. Furthermore, Rh and Pt are slightly enriched and Pd significantly depleted in the chromitites from the Hochgrössen massif (analyses 1 and 3 in Table 3 and Fig. 6a), whereas the chromitite from the Kraubath massif shows distinctive enrichment of Rh, Pt and in particular Pd (analysis 4 in Table 3 and Fig. 6a), if compared to typical chromitites from ophiolites and also to sample HG5. Values of 120 ppb for Rh, 940 ppb for Pt and 390 ppb for Pd are reached (Table 3).

(b) PGE in disseminated chromite-bearing serpentinite

The PGE distribution of one representative serpentinite with disseminated Cr-spinel from the Hochgrössen mas-

sif is so far available. Its pattern shows overall lower PGE concentrations than those of chromitites, i.e. about 0.01 times chondritic (sample HG8 – analysis 5 in Table 3 and Fig. 6a). Nevertheless, a slight enrichment of Rh and Pt with a corresponding depletion of Pd relative to Os and Ir becomes evident and is also reflected by the Ir/Pt ratio of 0.1 (Table 3, Fig. 6a). This is consistent with the general “unusual” trend of PGE patterns from chromitites.

(c) PGE in serpentinites

The PGE patterns of serpentinites illustrated in Fig. 6b, reflect the features shown by the “unusual” chromitites more distinctly. Serpentinites from the Hochgrössen massif are characterized by a continuously increasing pattern from Os to Pt and a significant depletion of Pd (analysis 6 in Table 3 and Fig. 6b). The patterns from the Kraubath serpentinites exhibit remarkable relative enrichment of Rh, Pt and in particular Pd (analyses 7–8

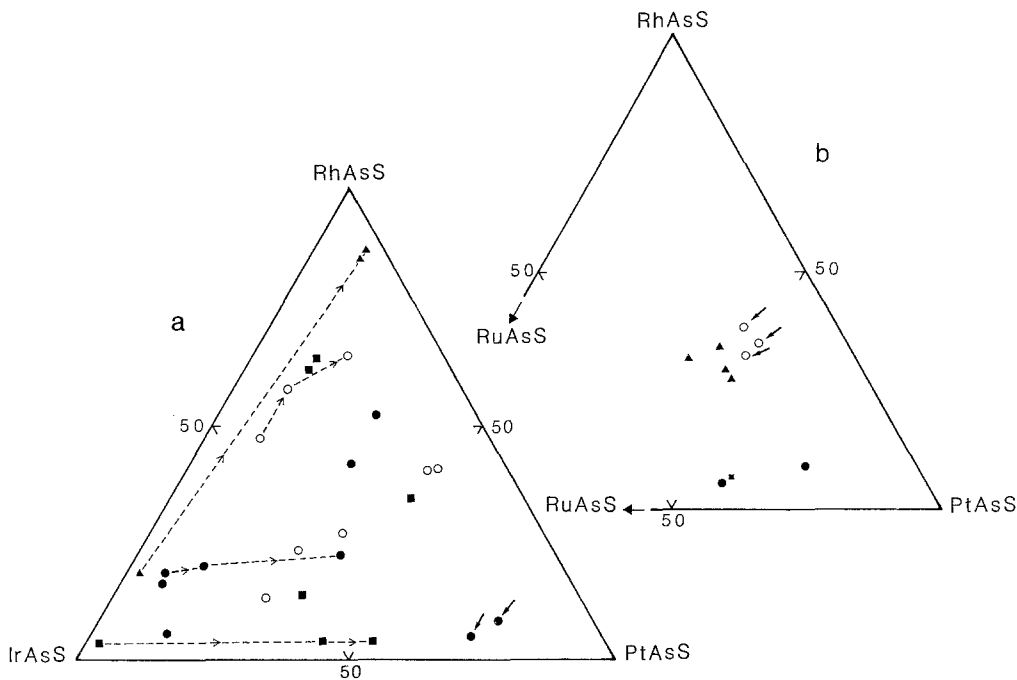


Fig. 8a, b. Chemical composition of platinum group sulfarsenides illustrated in (a) the RhAsS-IrAsS-PtAsS triangle. Dotted lines indicate compositional zonation within one mineral phase. Symbols: filled circles, inclusions within chromite core; open circles, inclusions in ferritchromite; filled squares, sulfarsenides interstitially; arrows indicate platarsite of type b (see text), and in b The RhAsS-

RuAsS-PtAsS triangle. Symbols with respect to location of sulfarsenides are the same as in a; arrows indicate platarsite of type a (see text); \times indicates platarsite of Thalhammer and Stumpfl (1988); filled triangles, platarsites from Onverwacht, Transvaal (Cabri et al. 1977)

in Table 3 and Fig. 6b). These patterns can be readily distinguished from those from both harzburgites and dunites from ophiolite complexes (Fig. 6b). They show more affinity to patterns of more highly differentiated rocks, i.e. from the cumulate sequence of an ophiolite complex (pattern DD in Fig. 6b – example taken from the Thetford Ophiolite, Quebec; Oshin and Crocket 1982), although the variable enrichment and depletion features are still clearly distinctive.

VII Platinum group minerals (PGM)

The PGM from the Hochgrössen and Kraubath massifs can be divided into four groups: (a) sulfides, (b) sulfarsenides, (c) arsenides and (d) alloys. Sulfarsenides and arsenides were found mainly as inclusions in altered chromite rims and interstitially together with silicates, whereas sulfides and alloys preferentially form inclusions within homogeneous chromite cores. The majority of PGM have been found in schlieren-type chromitites from both localities. The total volume as well as the number of different PGM phases identified so far in the Kraubath massif is by far less than that from the Hochgrössen. The amounts of different PGM phases and their occurrence with respect to its host are summarized in Table 2. Preliminary results on the PGM occurrence from the Hochgrössen massif have been given by Thalhammer and Stumpfl (1988).

(a) Sulfides

Cooperite (PtS) occurs rarely in ferritchromite rims or interstitially with silicates, and has been already reported by Thalhammer and Stumpfl (1988).

Laurite (RuS_2) is by far the most widespread PGM in both massifs. It preferentially occurs as inclusions in homogeneous chromite cores, however a few inclusions have also been found in ferritchromite rims. The grain size varies between 2 and 12 μm ; euhedral crystal shape is common (Fig. 6). It is commonly an isolated phase but can also be intergrown with other sulfide or sulfarsenides (Thalhammer and Stumpfl 1988). The chemical composition of laurite is marked by its variations in Ru, Os and Ir contents. Os can reach 23.8 wt% and Ir 9.0 wt%; chemical zoning has not been observed (Fig. 7). Laurite inclusions close to the edge of homogeneous chromite cores (at the contact of stage A and B of chromite alteration) and those within ferritchromite show a general preference for substitution of Ru by Os, Ir and Rh (Table 4). Two inclusions of an *Os-rich sulfide* with the approximate composition ($\text{Os}_{0.55}, \text{Ir}_{0.14}, \text{Ru}_{0.11}, \text{Rh}_{0.07}, \text{Pt}_{0.12}$) (S, As)₂ have been identified (Table 4) close to the margin of a chromite core and in a ferritchromite rim. Os is distinctly higher than (Ir + Ru + Rh + Pt) and hence erlichmanite is the possible phase.

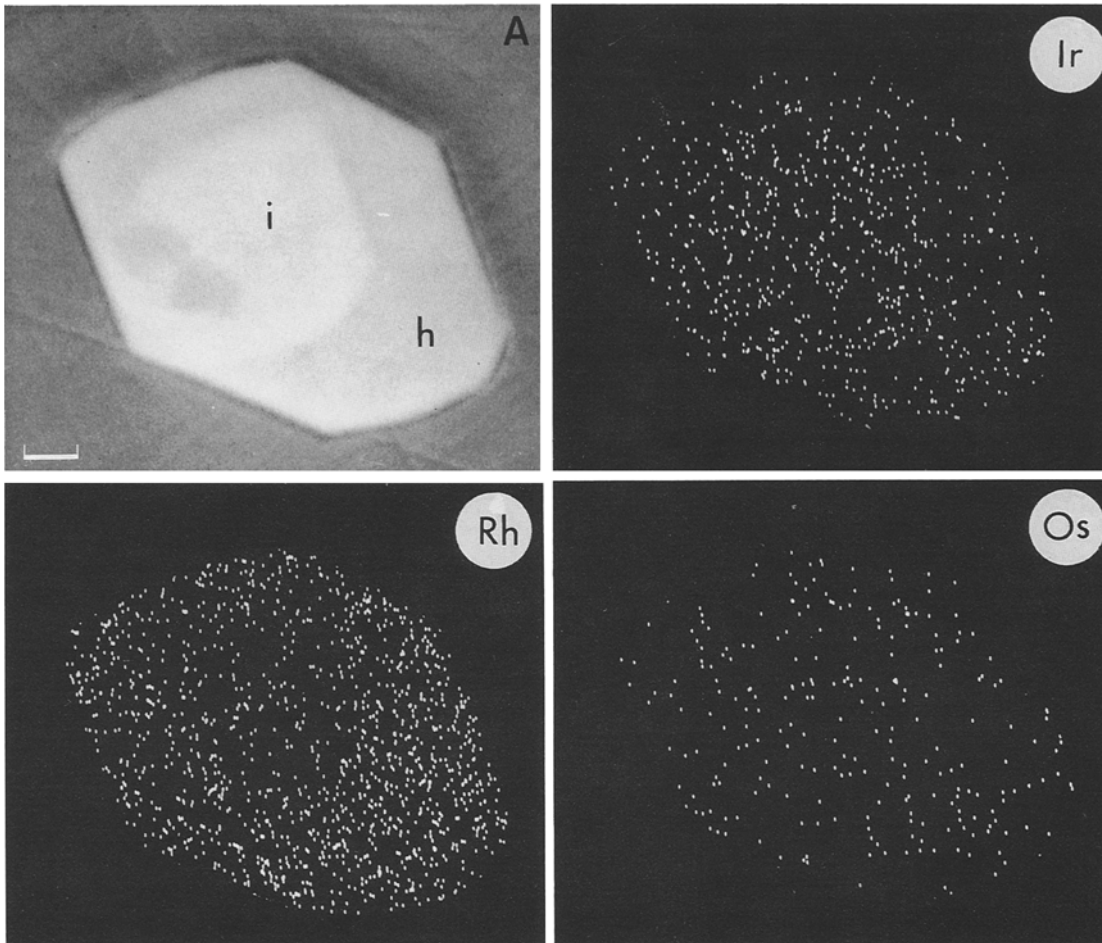


Fig. 9. Reflected-light photomicrograph (A) of an euhedral zoned irarsite-hollingworthite inclusion within inner rim of chrome-spinel (alteration stage B), and single element scans for *Ir*, *Ru* and *Os*.

The *centre part* of the inclusion is formed by irarsite (*i*) surrounded by hollingworthite (*h*). Scale bar refers to 1 μ

(b) Sulfarsenides

Sulfarsenides are rare from Kraubath and quite common in chromitites from the Hochgrößen (Table 2). Grain size varies between 3 and 10 μm . Inclusions within chromite cores and in ferritchromite commonly exhibit euhedral to subhedral crystal shape, whereas grains occurring interstitially with silicates are mainly irregularly shaped. The majority of sulfarsenides can be plotted in the ternary $\text{RhAs}-\text{IrAsS}-\text{PtAsS}$ system with intermediate chemical compositions (Fig. 8a). Single phase inclusions rarely exhibit almost end-member composition, i.e. *irarsite* (IrAsS), *hollingworthite* (RhAsS) and *platarsite* (PtAsS). *Irarsites* shows commonly zoning defined by increase of As, Rh, Pt and, less commonly, As, accompanied by a decrease in Ir (Table 4, Fig. 8a). In principle, irarsites occurring as inclusions in ferritchromite or interstitially, exhibit higher As, Rh and Pt contents than those within homogeneous chromite cores (Table 4).

Hollingworthite and *platarsite* occur predominantly in ferritchromite or as interstitial grains. *Hollingworthite*

commonly shows two-phase inclusions with irarsite in which irarsite forms the core surrounded by hollingworthite (Fig. 9).

Thalhammer and Stumpfl (1988) have already reported the occurrence of a Pt-rich sulfarsenide closely intergrown with laurite. During this study a few solitary Pt-rich sulfarsenide inclusions, one in a chromite core and three in ferritchromite have been found. Microprobe analyses demonstrated two types (Table 4): a) characterized by high Rh and Ru (10.4–10.8 at % and 4.8–5.1 at %, respectively), and b) marked by high abundances of Ru, Ir and As (4.2–10.1, 3.4–4.8 and 2.5–5.9 at %, respectively). Both types of PGM exhibit $\text{Pt} > \text{Rh}$ or Ru and $\text{Pt} > \text{Ru}$ or $\text{Os} + \text{Ir}$, and $\text{As} \sim \text{S}$. The first type shows obvious compositional similarities to the platarsite reported from Onverwacht, Transvaal, by Cabri et al. (1977) and can be considered as a member of the $\text{PtAsS}-\text{RuAsS}-\text{RhAsS}$ system (Fig. 8b). The second type, which includes the analysis of Thalhammer and Stumpfl (1988), indicates the existence of a natural Pt-dominated sulfarsenide corresponding to the PtAsS end-member (Fig. 8a).

One small (3 μm in diameter) irregularly shaped Pt-rich sulfarsenide grain was found interstitially. Apart from Pt which reaches 14.2 at %, it shows high Rh and Ir contents (11.5 and 6.5 at %, respectively) and a As/S ratio of 2.2. This As/S ratio indicates an intimate intergrowth of sperrylite (PtAs_2) and hollingworthite (RhAsS).

(c) Arsenides

Sperrylite (PtAs_2) is a common PGM in the Hochgrössen chromitites (Thalhammer and Stumpfl 1988). A few irregularly shaped (< 6 μm in diameter) grains have been also found interstitially with silicates in Kraubath. The chemical composition is nearly identical to those from the Hochgrössen massif, i.e. Os+Ir+Ru+Rh do not exceed 0.9 wt%. In places, sperrylite also forms inclusions in chromite cores and is then characterized by relatively high Ir (up to 8.2 wt%) and Rh contents (up to 6.0 wt%). Some of these inclusions exhibit close intergrowth with Pd–Sb–Pt or Pt-alloys. Two sperrylite-iridarsenite inclusions, occurring in ferritchromite rim, have been already reported from the Hochgrössen by Thalhammer and Stumpfl (1988).

(d) Alloys

Pd–Sb–Pt and Pt-dominated alloys, the latter containing in addition minor amounts of Os, Ir, Rh and Pd (Table 4), have been identified. They form small isolated inclusions in chromite cores (< 2 μm in diameter) or are closely intergrown with sperrylite. Alloys have only been found in chromite from Hochgrössen.

Two different groups of PGM inclusions become evident, which is in accordance with the distribution of silicate and sulfide inclusions: (1) Ru-Os-Ir-rich sulfides forming small (< 14 μm) randomly distributed inclusions predominantly within homogeneous chromite, and (2) PPGE-rich sulfarsenides and Pt-arsenides of variable crystal shape and grain size (3–30 μm) dominantly included in ferritchromite. The chemical composition of the latter is remarkably distinctive from subordinately occurring sulfarsenides and sperrylite inclusions in chrome-spinel cores (Table 4).

Discussion

Significance of chrome-spinel zoning

Both areas under consideration have undergone regional metamorphism of at least higher greenschist facies (El Ageed 1979). The first question to be answered is whether the compositional zoning of chromites is the product of progressive metamorphism, or alternatively, the chromite cores still represent a slightly modified relict of "primary" chrome-spinel. Generally, metamorphic

zoned chromites are characterized by a Cr-, Fe^{2+} -rich core and an Al-, Mg-rich rim (Evans and Frost 1975). Chrome-spinels from both the Hochgrössen and Kraubath massifs show quite the opposite, i.e. a large decrease of Al, Mg and Cr from core to rim (Fig. 2). Therefore, the chromite cores are considered to be the least altered part of the primordial chrome-spinel grain by the later processes of serpentinization and metamorphism. The high Cr/(Cr+Al) ratios and in particular the trends obtained in the Mg/ Fe^{2+} vs. TiO_2 diagram (Fig. 4) can be considered to be distinctive for podiform chromites.

The development of stages B and in particular C is clearly the result of serpentinization and metamorphism. The general compositional characteristics of these inner and outer rims of chrome-spinels are similar to those reported by Evans and Frost (1975) for metamorphic chromites (Fig. 2); a formation in a metamorphic range of upper greenschist to lower amphibolite facies is indicated. As a consequence, the grade of metamorphism seems to be higher in the Hochgrössen massif, i.e. frequent development of ferritchromite, which has been suggested already by El Ageed (1979). The irregular shapes of chromite cores indicate that alteration advanced from all directions. In chromitites the plane of alteration is commonly related to fractures.

The gradational element zonation within zones B and C indicates certain diffusion of elements during alteration. Mg, Al, Cr and perhaps also Fe^{2+} and Fe^{3+} diffuse out of the chromite. Secondary serpentine and chlorite phases occurring as inclusions in zones B and C exhibit high contents of Cr, and in places, Ni, giving indication for having accommodated these elements during chromite alteration.

The sharp boundary between stage B and C indicates that alteration of primary chrome-spinel can not be the only process responsible for the generation of ferritchromite and Cr-bearing magnetite. It strongly suggests that ferritchromite growth reflects a combination of dissolution of chrome-spinel and interaction with a metal-bearing fluid during serpentinization and metamorphism. Wylie et al. (1987) emphasized a "communication" between fluid and primary chromite. This fluid is responsible for both since it aids dissolution of chromite, and it contains metals, i.e. apart from elements such as Ni, Fe most likely also PGE, which were derived from the breakdown of primary silicate phases such as olivine and pyroxene, and primary sulfides.

Formation and significance of solid inclusions in chrome-spinel

Two different hypotheses have been postulated for the entrapment of mineral inclusions in primary chromite. With particular reference to silicates, the first model concluded that entrapment of inclusions is more or less contemporaneous with chromite magmatic precipitation (Talkington et al. 1984; Auge 1987; Lorand and Ceuleneer 1989). The second alternative hypothesis has been discussed in detail by Hulbert and Von Gruenewaldt

(1985) and Lorand and Cottin (1987), suggesting entrapment below the liquidus temperature of chromite during an extended period of post-magmatic annealing of the chromite ore in the presence of a fluid. Both models have been postulated on the basis of very different inclusion shape and distribution within the chromite host (summarized by Lorand and Ceuleneer 1989). Solitary inclusions without crystallographic orientation with respect to the chromite symmetry and with a tendency to spherical shape are indicative of post-magmatic entrapment during solid-state recrystallization of chromite, whereas orientated inclusions with respect to the chromite symmetry of negative crystal shape argue for entrapment during magmatic precipitation of chromite.

The silicate inclusions of the first group (olivine, orthopyroxene and amphibole) presented in this study do not provide enough criteria in favour of one of the two hypotheses. However, the discrete sulfide inclusions in chromite cores with lack of sulfide-first order silicate composite inclusions strongly suggest an entrapment during chromite crystallization from an immiscible sulfide liquid. The significant high Ni contents can be explained by subsequent subsolidus re-equilibration with the chromite host, whereby Fe is removed from the sulfides to fill vacancies in the chromite (Naldrett and Lehmann 1988). Their included occurrence in the rather unaltered chromite core protected them against secondary processes such as serpentinization and metamorphism, resulting in the compositional differences to corresponding interstitial sulfides.

The preponderance of Ru—Os—Ir-rich PGM inclusions is typical for ophiolitic chromitites (Talkington et al. 1984) and is well documented in both the Hochgrössen and Kraubath ultramafic complexes. The obvious lack of equivalent Ru—Os—Ir-dominated PGM apart from the chromite, might indicate that such PGM phases did not occur as cumulus phases and consequently had not been liquidus phases at the time of chrome-spinel precipitation. Following this assumption, PGM phases must have been formed prior to or after the precipitation of the chrome-spinel. An origin of PGM prior to chromite has been proposed by many authors (summarized in Talkington et al. 1984). The probability of early precipitation of Ir—Ru—Os dominated PGM in a basaltic liquid at 1430° C prior to the formation of chromite has been shown also experimentally by Amossè et al. (1987). However there is not enough evidence to reach a conclusion whether the PGM inclusions in chromite cores from the Hochgrössen and Kraubath massifs were entrapped as immiscible Ru—Os—Ir alloys and/or sulfides during the precipitation of chromite or during later processes described herein.

The solid inclusions in ferritchromite and interstitial mineral grains clearly show a secondary origin related to serpentinization and metamorphism.

The occurrence of (1) abundant PPGE-rich sulfarsenides and arsenides, (2) sulfides dominated by galena, pyrite and arsenopyrite, both as inclusions in ferritchromite, as well as forming discrete mineral phases interstitially in both massifs, and (3) the local variability of

PGM in abundance, i.e. frequently with a remarkable preponderance of PPGE-rich sulfarsenides and arsenides over IPGE-dominated sulfides (Table 2), is quite unique and unusual for typical ophiolitic chromitites. Rare appearance of PPGE-rich sulfarsenides and arsenides as inclusions in rather unaltered chromite has been reported from Southwestern Oregon (Stockman and Hlava 1984), Vourinos (Auge 1985), North Tibet (Yu and Chou 1979), Northwestern China (Chang et al. 1973), and with a greater variety from the Shetland ophiolite (Prichard et al. 1987). Lorand and Ceuleneer (1989) have shown that sulfides enclosed in unaltered chromite are composed of pentlandite, heazlewoodite and millerite, whereas galena, pyrite and arsenopyrite are lacking.

Sympathetic with the distribution of PGM, the PGE patterns clearly reflect the remarkable abundance of PPGE-rich sulfarsenides and arsenides. The local variability of PGE distribution, ranging from patterns typical for ophiolitic chromitites to most unexpected patterns characterized by enrichment and/or depletion in PPGE (Fig. 6) can not be explained by magmatic processes, such as degrees of melting and/or fractionation (Barnes et al. 1985). This evidence strongly suggests a secondary redistribution of PGE and secondary formation of PGM during serpentinization and metamorphism. Similar conclusions have been drawn by Economou and Naldrett (1984) during the investigation of the sulfide mineralisation hosted in podiform chromitites from Eretria, Greece. A precipitation of sulfides by hydrothermal fluids, responsible for the serpentinization has been proposed on the basis of geochemical data including "unusual" PGE pattern marked by a depletion in Pd. Prichard et al. (1987) reported from the Shetland ophiolite both PGE pattern typical for ophiolite complexes as well as those showing a jagged distribution with relative enrichment of Pt and/or Pd; however no conclusive explanation has been given.

Several studies on the behavior of PGE in hydrothermal environments have shown that in particular Pt and Pd are more soluble and can be more easily transported than the other PGE (Keays et al. 1981; Seccombe et al. 1981; Leshner and Keays 1984; Barnes et al. 1985; and also summarized by Stumpfl 1986). Mountain and Wood (1988) pointed out that chloride, hydroxide and bisulfide are the ligands considered most likely to contribute to Pt and Pd transport at temperatures around 300° C and above, temperatures which have to be considered during the secondary events from the Hochgrössen and Kraubath. Furthermore, the same authors stressed that an oxidizing and acidic fluid would be required to transport Pt, Pd as chloride complexes, whereas hydroxide and/or bisulfide complexes become much more important in a less oxidizing, neutral or even alkaline and As—Te-poor chemical environment. The latter environment is most likely applicable to the conditions during serpentinization and metamorphism at the Hochgrössen and Kraubath for the following reasons:

(1) Chlorite as inclusion in ferrite-chromite, as well as a secondary interstitial phase is quite common in both massifs. Chlorite, the dominant hypogene alteration

product, is stable at pH values greater than 4.0 (Beane and Titley 1981; Mountain and Wood 1988).

(2) There is an obvious lack of hematite as an alteration product. The typical interstitial ore mineral assemblage is pyrite-pyrrhotite-magnetite (El Ageed 1979). This strongly indicates that the fluid had a f_{O_2} far below the hematite stability field.

(3) As contents, typical for accompanying the hydrothermal circulations responsible for serpentinization, have been rather low if compared to other serpentinized ultramafic portions of ophiolites (Leblanc and Billaud 1982; Foose et al. 1985; Thalhammer et al. 1986). As-phases are, apart from PPGE-rich sulfarsenides and sperrylite, very rare at both areas under consideration (El Ageed 1979; this study).

(4) It has been shown by Poty et al. (1972) and Rucklidge and Patterson (1977) that the process of serpentinization of olivine considerably increases the pH of the solution, hence solutions emerging from serpentinites are invariably alkaline.

As a consequence it is proposed that PPGE particularly Pt and Pd were transported as bisulfide and/or hydroxide complexes under low f_{O_2} (perhaps around -36 , Mountain and Wood 1988), sulfur-rich conditions and at neutral to alkaline pH. The PPGE were possibly accompanied by metals like Ni and Cu. Furthermore, it is suggested that deposition of PPGE, Ni and Cu has taken place due to reaction of the fluid with chromite, leading to the formation of PGM, sulfides and occasionally arsenides which were either trapped by the simultaneously generated ferritchromite or have filled the interstitial space together with secondary silicates. A drop in temperature may have played an additional role because the solubility of bisulfide complexes is temperature dependent, i.e. decrease in temperature causes decrease in f_{O_2} (Mountain and Wood 1988). Iron is not particularly mobile in bisulfide solutions (Crerar and Barnes 1976), thus it is not likely that Fe has been transported in the same mode as the PPGE, Ni and Cu. However Cl contents in serpentine indicate that the fluid contained a considerable amount of Cl. Apart from the fact that Fe is liberated during the alteration of chromite, it is thus assumed that Fe has been transported as a hydroxy-chloride phase in the same chemical environment as stated above.

Foose et al. (1985) described sulfide occurrences in cumulus pyroxenite from southwestern Oregon, clearly showing a magmatic origin, and characterized by a strong enrichment of PPGE and Au. A sharp drop in the PPGE concentrations were ascertained, where these sulfides suffered serpentinization. This might give a vague indication of a derivation of PPGE from primary sulfides which have been remobilized during serpentinization. Further support for this proposal is obtained by the "clean" chemical composition of secondary pentlandites, in particular with respect to very low Pd contents if compared to pentlandite inclusions in chromite cores (Table 1).

The influence of serpentinization and metamorphism on the PGE distribution in the Hochgrössen and Krau-

bath massifs is thus regarded as a general concentration process, leading to the formation of new PGM (sulfarsenides and arsenides). The intensity of this process varies locally, depending on the availability of elements, fluid compositions and conduits. Gold enrichment is an additional typical feature of hydrothermally remobilized and/or deposited mineralizations found in ophiolites (Economou and Naldrett 1984; Foose et al. 1985). The Hochgrössen and Kraubath massifs are lacking in Au-enrichment (Fig. 6). It can be only assumed that either the primary sulfides, possibly representing the source for PGE, were very low in Au, or the gold has remained in the hydrothermal fluid, to be deposited elsewhere.

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