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Major, trace, noble and rare earth element distribution in polymetamorphic ultramafic rocks (Aar massif, Central Alps, Switzerland)

by *Giuseppe G. Biino*[1] and *Thomas Meisel*[2]

Abstract

In this contribution major, minor, trace, rare earth and noble elements are investigated in order to constrain the chemical evolution of four representative ultramafic rock enclaves within the Aar massif.

The presence of the ultramafic rocks in the Aar massif is related to one of the earlier, but poorly understood tectonic events. The ultramafic rocks are associated with metagabbros and/or polymetamorphic mafic rocks. Mineralogically the ultramafic rocks now consist mainly of secondary phases. Crustal (serpentinization) and mantle (melt/rock interaction) processes are characterized on geochemical grounds. During serpentinization several elements were probably remobilized. Rare earth elements (REE) preserved a chondritic concentration and were possibly not (or only slightly) affected by serpentinization. It is suggested that platinum group elements (PGE) were essentially immobile during serpentinization. Since PGE, Ni, Sc, Co were not remobilized, their concentrations are used to determine the magmatic petrogenesis of the ultramafic rocks. The Ni/Co ratio appears to be a valuable criteria to recognize the magmatic evolution of the ultramafic rocks. There is no covariance between REE and PGE concentrations. On the basis of PGE concentrations, the investigated rocks are interpreted as residues from partial melting (group I; depletion of PPGE) and cumulate (group II; depletion of IPGE) which have later been contaminated by a Pt-Pd and light rare elements enriched melt. Other trace element data support this model.

A chemical affinity with the ultramafics occurring in the Gotthard massif is demonstrated. Lithostratigraphic and chemical information helps us to understand the evolution of polymetamorphic ultramafic rocks from oceanic genesis to accretion into continental crust along an active margin.

Keywords: ultramafic rocks, platinum group elements, neutron activation analysis, mantle petrogenesis, Aar massif, Central Alps.

1. Introduction

Ultramafic rocks make up part of orogenic belts of all geological ages. The presence of such ultramafic rocks in the crystalline basement was for a long time considered mysterious. It turned out that ultramafic rocks were either fragments of upper mantle, cumulates from mafic magma (generated in different tectonic setting, both oceanic and continental) or more rarely crystallization products of ultramafic magmas.

The ultramafic rocks witness the mantle-crust interactions responsible for crust generation. Despite the simple chemistry of the rocks and rock forming minerals they can provide information relevant to the petrotectonic setting. In several cases, it is possible to distinguish between the different genesis and tectonic settings, since systematic compositional and mineralogical properties are described from the different environments (BONATTI and MICHAEL, 1989; NICOLAS, 1989). However, the geochemistry of ultramafic rocks is not always closely related to their tectonic setting as generally believed. Notable variations due to mantle heterogeneity are also documented. Subcontinental mantle has been described in the Atlantic ridge (BONATTI et al., 1992), and in an oceanic environment the MOR basalts do not represent all the lavas. The presence of oceanic island basalt may reveal the existence of at least three

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other mantle sources interacting with the depleted oceanic mantle (i.e. EM1, EM2, HIMU; Hart, 1988).

Beside this possible primary heterogeneity, preservation of ultramafic rocks in polycycle metamorphic basements unfortunately does not mean a preservation of their primary chemical and mineralogical composition or fabric. Crustal metasomatism makes it difficult to investigate these rock types, and this suggests that the ultramafic rocks are only potentially good markers of lithosphere evolution. Nevertheless, chemical characterization of the protoliths may be possible when several elements are taken into account, and the integration of the chemical information with the other data (field, petrographic, petrologic) can still help to constrain the geodynamic event responsible for ultramafic rocks genesis and crustal emplacement, even in polymetamorphic basement.

Since the discovery of peridotitic lavas in Precambrian terranes, the genesis of ultramafic rocks cropping out in old basements must be reconsidered. Therefore, the presence of peridotitic magma in the Central Alps must be supported or discarded only after a proper investigation.

The present contribution reports a geochemical investigation of four ultramafic samples from the Aar massif of the pre-Variscan Helvetic basement (Central Alps). The aim of this work is to evaluate the chemical evolution and element mobility during both mantle and crustal processes. The chemistry of these ultramafic rocks is discussed in parallel with komatiite and oceanic equivalents in order to assess the significance of the observed composition. A comparison with ultramafic rocks cropping out in the Gotthard massif (Biino and Meisel, 1993) is also discussed in order to figure out similitude and difference between these two Helvetic basements.

2. Geological setting

2.1. LOCATION, GENERAL SETTING AND AGE

The Aar-, Tavetsch- and Gotthard massifs (Helvetic massifs) constitute pre-Variscan basement in the Central Alps of Switzerland, which is partially reworked by the Variscan and Alpine orogeneses (Figs 1, 2). General reviews of the geology of the Helvetic massifs are given by Abrecht et al. (1991), von Raumer et al. (1993) and in several contributions in this volume.

This contribution is centered on the ultramafic rocks from the Aar massif, the northernmost Helvetic massif of the Central Alps. In his review of more than 100 years of geological research on this massif, Abrecht (1994) documented its complex structural and metamorphic evolution, and proposes a new interpretation of this part of the European basement.

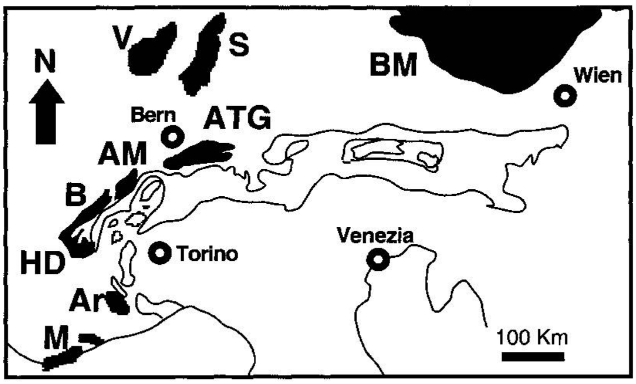

Fig. 1 Aar-, Tavetsch- and Gotthard massifs (ATG) and the External Massifs (Ar = Argentera massif; HD = Haut Dauphiné massif; B = Belledonne massif; AM = Aiguilles Rouges and Mont Blanc massifs) and their location relative to the closer european basement (M = Maures Esterel massifs; V = Vosges; S = Schwarzwald; BM = Bohemian massif).

The Aar massif contains sparse ultramafic rocks. The presence of the ultramafic rocks in this basement is problematic as there are no obvious explanations for their crustal emplacement. They are everywhere associated with mafic rocks, and cogenetic relations are highly probable. The mafic-ultramafic rocks form mappable discontinuous lineaments that can be followed along the regional NE–SW (Variscan) strike direction (Fig. 2). These lineaments are not randomly distributed in the Aar massif, but the mafic-ultramafic rocks show strong affinity to a particular supracrustal unit, which represents the oldest part of the basement. They conclude that this unit is probably related to one of the earlier tectonic events (pre-Ordovician).

The ultramafic rocks occur as lenses (up to few tens of metres long) included both in a migmatitic terrane and in detrital sequences. The migmatitic terrane locally looks like a pegmatitic intrusive tonalitic in composition (e.g. Ofenhorn-Stampfhorn unit, after Abrecht, 1980; Massaschlucht area, after Labhart, 1965; or in the Etzli Valley, after Pflugshaupt, 1927). The detrital sequences locally preserve flyschoid structures and are made up of gneissic metapelites, metapsammites, calc-silicate rocks and quartzites (e.g. Silberberg series at Sustenpass and Lötschen Valley). From field observations, a derivation of the ultramafic rocks of the Aar massif from mantle xenoliths in magmatic bodies or a cogenetic origin with

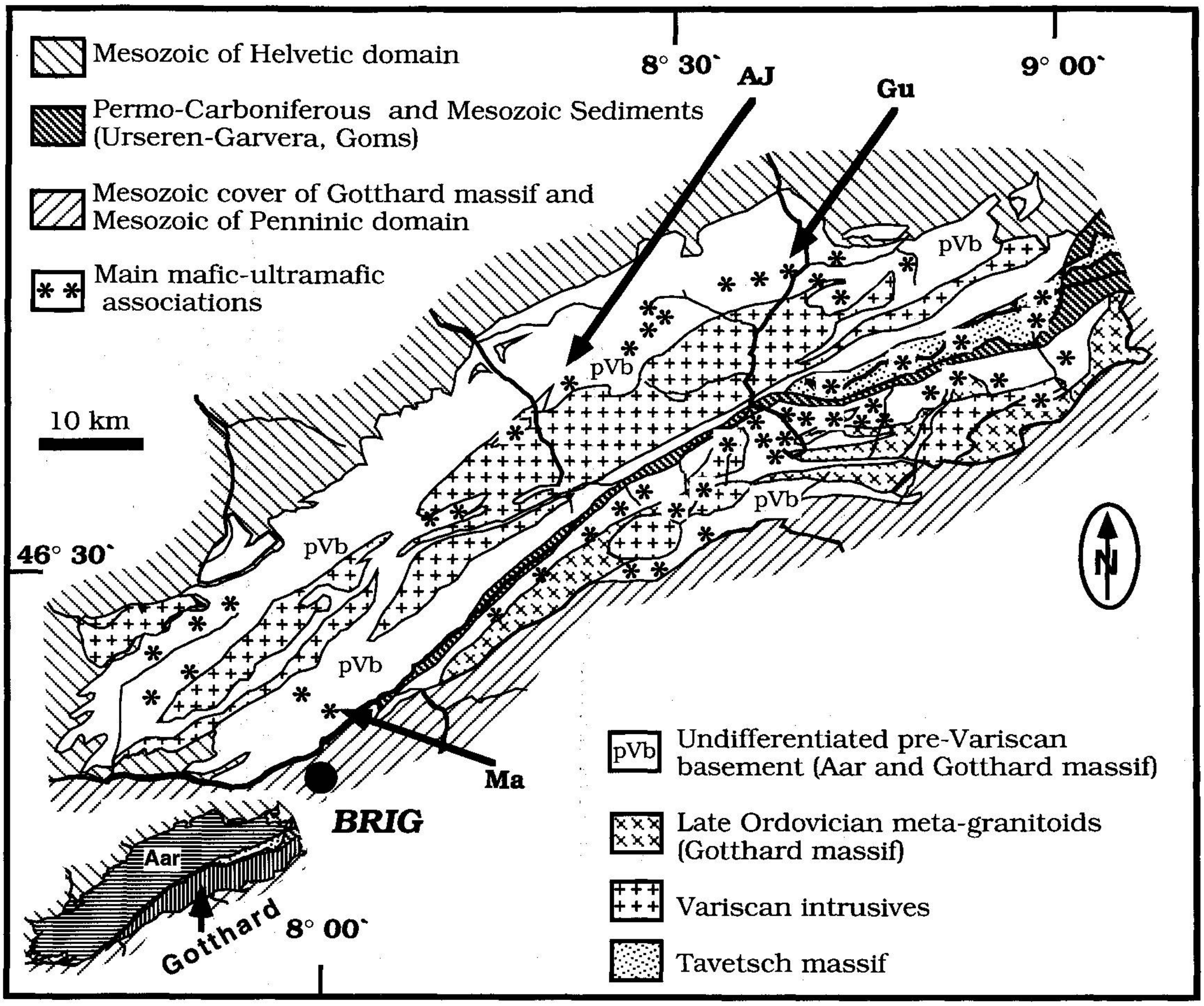

Fig. 2 Schematic geological map of the Helvetic massifs. The pre-Variscan basement is undifferenciated, but the larger mafic-ultramafic lenses are reported and specifications are given for the sample locations.

Variscan plutonic rocks is not possible. On the other hand, ultramafic lavas which have flowed onto the metasedimentary sequence cannot be excluded.

In the Lötschen Valley and at the Sustenpass the lithostratigraphic sequence as a whole shows striking analogies with the oldest part of the Gotthard massif (MERCOLLI et al., 1994). The field association is reminiscent of an *ophiolite* terrane embedded in an accretionary wedge sequence (ABRECHT et al., 1991). BIINO et al. (work in progress) suggested that an accretionary wedge in the Gotthard massif formed from late Proterozoic (Riphean?) to lower Palaeozoic. In the Aar massif there are no clear time indications, but Cambrian or Late Proterozoic ages are compatible with isotopic data (STILLE, 1992, pers. comm.; SCHALTEGGER, 1993).

Field observation suggests that the ultramafic rocks embedded in migmatites and in pegmatitic rocks were part of the basement before the migmatitic event. Migmatites are intruded by orthogneiss (LABHART, 1965; ABRECHT, 1993) possibly Late Caledonian in age. The age of the high temperature event is quite controversial, but probably the migmatitic event is at least Lower Ordovician (SCHENKER and ABRECHT, 1987; SCHALTEGGER, 1993).

2.2. STRUCTURAL AND METAMORPHIC FRAMEWORK

The Aar massif experienced a protracted history of deformation and metamorphism during several tectonic cycles extending from the Upper

Tab. 1 Sample, locality, approximate coordinate, and mineralogy of the investigated ultramafics.

Sample #	Locality	Approximate coordinate	Mineralogy
Ma3	Massa	642 700 / 133 100	srp, tlc, ore
AJ1083	Haslital	erratic block	ol, tlc, opx, srp, tr, chl, sp, ore
Gu4	Gurtnellen	690 900 / 176 500	tr, phl, sp, tlc, chl, crm, ore
Gu5	Gurtnellen	690 900 / 176 500	tr, phl, sp, tlc, chl, crm, ore

Proterozoic to the present (LABHART, 1965; STECK, 1966; SCHENKER and ABRECHT, 1987; ABRECHT and SCHALTEGGER, 1988; ABRECHT, 1994; SCHALTEGGER, 1994). The relative chronology used below is adapted from ABRECHT et al. (1991; ABRECHT, 1994).

The associated mafic rocks show pre-migmatitic compositional banding and rootless isoclinal folds. The pre-migmatization mineral assemblages are usually overprinted by the later metamorphic events. Garnet (the most stable phase of the older paragenesis) is usually replaced by the assemblage biotite + plagioclase ± epidote. A former high pressure event is possible (e.g. rutile-bearing symplectite garnet amphibolite at Sustenpass), but Na-cpx is not preserved. In the Massaschlucht area, amphibole is replaced by biotite during migmatization.

The Variscan metamorphic event occurred under low amphibolite or greenschist facies conditions. The Alpine metamorphic event affected the northern part of the massif at very low metamorphic grade (pumpellyite-stilpnomelane). Toward the contact with the Gotthard-Tavetsch massifs the metamorphic grade increases up to greenschist facies conditions (NIGGLI and NIGGLI, 1965; NIGGLI, 1970; FREY et al., 1980).

In the Aar massif the ultramafic rocks occur as serpentinites containing relics of higher temperature phases (Tab. 1). A clear correlation between metamorphic cycles and blast-growth events is difficult. The high temperature phases are pre-Late Variscan. The ultramafic rocks have been affected by metamorphic conditions of greenschist facies and even lower grade at the end of every pre-Alpine cycle and during Alpine orogeny. Therefore, the serpentinization is not necessary Alpine in age.

3. Petrography of the ultramafic rocks

It is reasonable to interpret all the ultramafic rocks as belonging to a single group, although with the risk of comparing ultramafic rocks very different both in age and origin. This risk cannot be avoided because the present knowledge on the Aar massif geology is still incomplete, and Variscan intrusive and tectonic activity has disrupted the lithostratigraphy (ABRECHT, 1994).

In this contribution ultramafic rocks are described which are associated with mafic rocks and embedded in the migmatite terrane (or in the related pegmatoid intrusives). The selected localities were investigated in detail and it has been possible to prove that the mafic and ultramafic lenses were part of the basement lithostratigraphy before the migmatitic event. All the ultramafic lenses considered are locally hydrothermally altered along the contact with the country-rocks. The smaller bodies (several centimetres to metres) are transformed into bladed actinolite fels surrounded by greenish micaschists (containing Cr-bearing muscovite). The larger lenses show a metasomatic zoning. The highly metasomatized rim portions of the lenses were not investigated, and the analysed samples were collected from the homogeneous core.

3.1. DESCRIPTION OF THE INVESTIGATED ULTRAMAFIC ROCKS

Detailed petrologic studies of our analysed samples or related samples are currently in progress, and only brief petrographic descriptions are presented here. The precise locations of the samples are reported in table 1.

Two samples (Gu4, Gu5) were collected in the ultramafic lens cropping out along the Reuss river not far away from Gurtnellen. In this locality the ultramafic lens shows a compositional layering in metre scale made up by massive (Gu4) alternating with spinifex-like (Gu5) ultramafic rocks. The acicular crystals of the spinifex-like metamorphic textures are tremolite, or anthophyllite, or talc + magnesite + magnetite (replacing anthophyllite). Few chromite crystals are still preserved in the core of spinels.

Sample AJ1083 is part of an erratic block in the Ofenhorn Stampfhorn unit (collected by J. ABRECHT, 1991). The country rock of this sample is probably a migmatite of tonalitic composition.

Sample Ma3 was collected at the Massaschlucht. The ultramafic lens is included in an augen-gneiss. It is a massive serpentinite containing acicular pseudomorphoses (after orthopyroxene or orthoamphibole) made up by serpentine + magnetite.

4. Analytical techniques

4.1. SAMPLE PREPARATION

From each sample 4–5 kg were crushed in a jaw crusher. The gravel was split into 0.5 kg portions and one part was ground for 10 seconds in a carborundum mill. The powder was split into 200–300 g aliquots and one part was ground again for 15 seconds in the same mill. The following analytical methods were applied.

4.2. PLATINUM GROUP ELEMENTS

A NiS fire assay preconcentration procedure with a subsequent neutron activation (NAA) was chosen to determine the platinum group elements and gold (PGE). The method was adapted from (Robért et al., 1971) using lithium tetraborate which we found to have a lower blank than sodium tetraborate. The PGEs of 11 and 25 g of the powdered rock were collected in 5 g and 10 g NiS buttons respectively. The bead was directly dissolved in 6M reagent grade HCl under N_2 over night. Because of this dissolving step at elevated temperature and the longer time period, the chemical yield was lower. From a comparison with tracers, only the more soluble PGEs (Pt, Pd and Au) were affected. The filtered residues were irradiated for 1.85 hours in a neutron flux of 3×10^{13} cm^{-2}s^{-1} at the SAPHIR reactor at the Paul Scherrer Institut in Würenlingen (CH). Palladium could be detected in a first counting step 16 hours after EOB (end of burn). Ruthenium, Os, Ir, Pt and Au were counted one week and three weeks after. Errors are the 1σ error of the measurements taking into account chemical yield, counting statistics, and other accountable errors. The chemical yields used for calculations were 90% for Os, Ir, Ru, 60% for Pt and Au and 50% for Pd. Therefore the values for Os, Ir and Ru have the highest precision with an average relative error below 10%. The results were corrected for chemical yield and for blank. Platinum results had to be corrected for the ^{199}Au contribution of gold since the neutron flux was high. For comparison we analysed a chromitite reference sample CHR-Pt+ (Potts et al., 1992). Our analysis is in good agreement with the recommended values reported (Tab. 2).

Tab. 2 Accuracy of noble metal analysis on chromite reference sample CHR-Pt+ (literature values after Potts et al., 1992).

	Literature [ppm]	This work [ppm]
Au	4.3° ± 0.75	4.4 ± 0.3
Ir	6.2° ± 0.83	6.2 ± 0.5
Os	1.9* ± 1.30	2.0 ± 0.2
Pt	58.0° ± 6.69	60.2 ± 6.0
Ru	9.2° ± 2.00	9.6 ± 0.9

° recommended value
* proposed value

4.3. MAJOR, TRACE AND RARE EARTH ELEMENTS (REE)

Analysis of SiO_2, TiO_2, Al_2O_3, MgO, MnO, CaO and Ni were performed by standard X-ray fluorescence (XRF) techniques (Nisbet et al., 1979). For an estimation of the accuracies we refer to Stern (1972) and to Reusser (1987). The XRF analysis were performed at the University of Fribourg. Loss-on-ignition (L.O.I.) represents weight loss measured after heating the pre-dried (110 °C for 24 hours) sample powders at 1000 °C for 30 minutes.

50 to 100 mg sample were irradiated in suprasil quartz vials for 1.85 hours in a thermal neutron flux of 3×10^{13} cm^{-2}s^{-1}. The gamma radiation of the samples was measured 1–2 days, one week and 3 to 4 weeks after EOB. Dead times were low because of the low sodium abundance. BHVO-1 was used as a monitor. An empty vial was also irradiated for blank corrections. Special care was taken of the counting statistics of the REE. The fission contribution of ^{235}U was lower than 10% in most cases. Uncertainties of instrumental neutron activation of REE are known to be problematic but still the data were used for evaluation. Europium was counted several times up to one year after EOB. The 1σ errors for REE are below 15%. All elements presented are above determination limit after Currie (1968) except Lu in some samples. The 1σ errors for Co, Zn, Fe, Sc, and Cr are below 8%.

5. Results

The major, trace and noble element analyses of the investigated samples are given in table 3. Al-

Tab. 3 Major, trace, noble and rare earth elements abundances for the ultramafics. Samples from the Gotthard massif (Biino and Meisel, 1993) are included in the statistic. Primitive mantle values are after Brügmann et al. (1987).

[wt%]	Ma3	AJ1083	Gu4	Gu5
SiO_2	50.62	56.04	49.35	53.12
TiO_2	0.01	0.10	0.06	0.04
Al_2O_3	1.35	3.17	5.36	2.97
FeO	5.55	5.11	5.87	5.05
MnO	0.12	0.15	0.12	0.14
MgO	42.30	31.94	32.92	30.85
CaO	0.05	2.25	5.70	7.39
L.O.I.	11.16	4.62	7.37	6.19
[ppm]				
Na	< 500	582	1251	1184
K	150	4360	1941	1478
Sc	10.3	10.6	15.2	12.2
Cr	2513	2627	4623	3429
Co	109	85	109	83
Ni	2005	1423	1621	1174
Zn	71	105	75	47
Ga	2.7	4.4	4.3	1.3
As	< 1	< 1	< 1	1.1
Sb	0.2	2.2	< 0.2	0.2
Th	< 0.1	< 0.1	< 0.1	< 0.1
La	0.64	0.34	0.07	0.28
Ce	1.05	0.93	0.19	0.91
Sm	0.19	0.15	0.11	0.2
Eu	0.043	0.038	0.046	0.070
Tb	< 0.01	0.04	0.01	0.03
Yb	0.03	0.34	0.29	0.28
Lu	< 0.03	0.07	0.03	0.06

[ppb]	Ma3	AJ1083	Gu4
Ru	8.3 ± 1.0	2.6 ± 0.4	6.4 ± 0.8
Pd	< 2	35.8 ± 3.1	16.7 ± 2.6
Os	4.1 ± 0.4	1.8 ± 0.2	3.0 ± 0.3
Ir	3.8 ± 0.2	0.9 ± 0.0	2.2 ± 0.1
Pt	13.3 ± 2.4	16.9 ± 2.9	8.4 ± 1.7
Au	4.1 ± 0.4	9.4 ± 1.0	2.2 ± 0.2
Ratio/Ir	Ma3	AJ1083	Gu4
Ru	2.2	2.8	2.9
Pd		38.5	7.7
Os	1.1	2.0	1.4
Ir	1.0	1.0	1.0
Pt	3.5	18.1	3.5
Au	1.1	10.1	1.0
AVG	Mantle	Group I Stdev	Group II Stdev
Ru	4.3	6.7 ± 1.9	4.4 ± 1.9
Pd	4.0	6.6 ± 2.9	21.5 ± 12.6
Os	3.3	4.0 ± 1.0	2.4 ± 0.6
Ir	3.6	3.7 ± 0.7	1.3 ± 0.7
Pt	10.0	10.4 ± 3.9	14.4 ± 5.3
Au	1.0	2.7 ± 2.4	5.7 ± 3.0
PGE/Ir	Mantle	Group I Stdev	Group II Stdev
Ru	1.2	1.9 ± 0.8	2.0 ± 1.4
Pd	1.1	2.2 ± 1.2	22.1 ± 15.5
Os	0.9	1.1 ± 0.2	1.2 ± 0.8
Ir	1.0	1.0 ± 0.0	1.0 ± 0.0
Pt	2.8	2.9 ± 1.1	13.5 ± 7.3
Au	0.3	0.7 ± 0.6	6.0 ± 4.7

teration and weathering processes have clearly changed several times the original abundance of H_2O, carbonates, and the primitive Fe^{3+}/Fe^{2+} ratio. Therefore, we adjusted all the analyses to a volatile-free, reduced-iron basis. In the following the platinum group elements and gold (PGE) are subdivided into the IPGE (Os, Ir, Ru) and the PPGE (Rh, Pt, Pd and Au).

On geochemical reasons the ultramafic rocks can be separated in two groups. Ma3 makes up the first group. The other samples (Gu4, Gu5, AJ1083) form the second group.

5.1. NORMATIVE COMPOSITION

Characterization of the primary protolith is hardly possible because the original mineralogy has been obscured by recrystallization whithin the crust. However, if the metamorphism was isochemical, then it is possible to infer the protolith from the chemical composition. According to their normative composition (CIPW norm) the samples Gu4 and Gu5 are olivine websterite, AJ1083 is a websterite, and Ma3 is a harzburgite (Fig. 3).

5.2. MAJOR AND TRACE ELEMENTS

First group: The sample Ma3 shows concentrations of the most incompatible components (Fe, Ti, Al, Ca) below the estimated concentrations for the upper mantle (Maaløe and Aoki, 1977; Jagoutz et al., 1979) and model pyrolite (Ringwood, 1979). Calcium (Fig. 4) is depleted even in comparison to an oceanic harzburgite (Dmitriev et al., 1976). The Mg number ($Mg/Mg+Fe_{tot}$) is 90.8. Apart from silicon concentration, major elements in Ma3 do not show any enrichment due to contamination with the surrounding gneissic rock.

The Ni/Co ratio is 18.1. The ratio is comparable to that observed in the peridotites of the Gotthard massif (17.9 ± 1.5; Biino and Meisel, 1993).

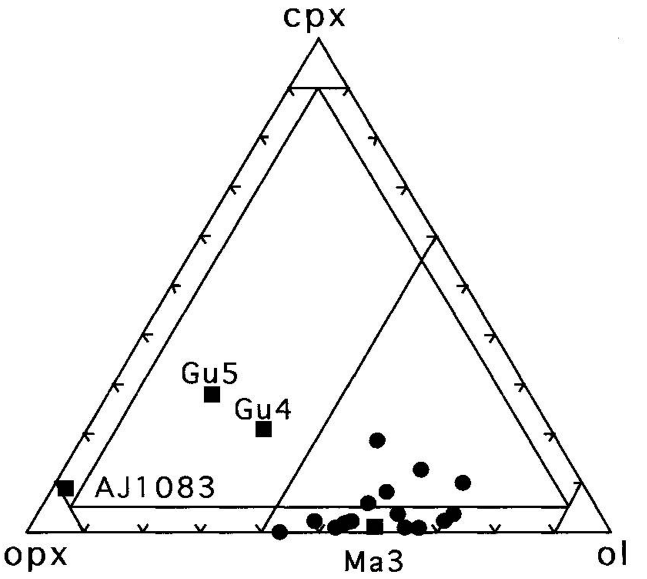

Fig. 3 CIPW normative proportion of Aar (squares) and Gotthard (dots) ultramafic rocks. The nomenclature is that recommended by the I.U.G.S. Subcommission on the systematics of igneous rocks.

Second group: The samples AJ1083, Gu4, Gu5 show a limited range in the Mg number (88.60 ± 0.28), but silicon is anomalous high in sample AJ1083. These samples are compared in figure 4 with a pyroxenite from Zabargad island (sample Z-31, table 1, pag. 143 in Piccardo et al., 1988). A depletion in Ti and Al (Gu5, AJ1083) and an enrichment in Ca (Gu4, Gu5) is evidenced by this comparison. Cobalt, Sc and Cr are below the values detected for the pyroxenites of the same island. The range of chemical variability of pyroxene-rich ultramafic rocks is large and the investigated samples show compositions still comparable to values found in the literature (Frey and Prinz, 1978; McDonough and Frey, 1989). The Ni/Co ratio is variable (AJ1083 = 16.8; Gu4 = 14.9; Gu5 = 14.1) and intermediate between the value of carbonaceous chondrites (22.21 ± 1.12; Kurat et al., 1980) and pyroxene-rich peridotites of the Gotthard massif (12.2 ± 1.1, an ultramafic rock cumulated from a basaltic melt has a ratio of 5.5; Biino and Meisel, 1993). In sample AJ1083 and Gu4, Ga is higher than in the average concentration of the ultramafic rocks in the Helvetic basement (2 ± 1, n = 19; Biino and Meisel, 1993), but the observed Ga abundances are in the range of mantle peridotites (Frey et al., 1985).

5.3. RARE EARTH ELEMENTS (REE)

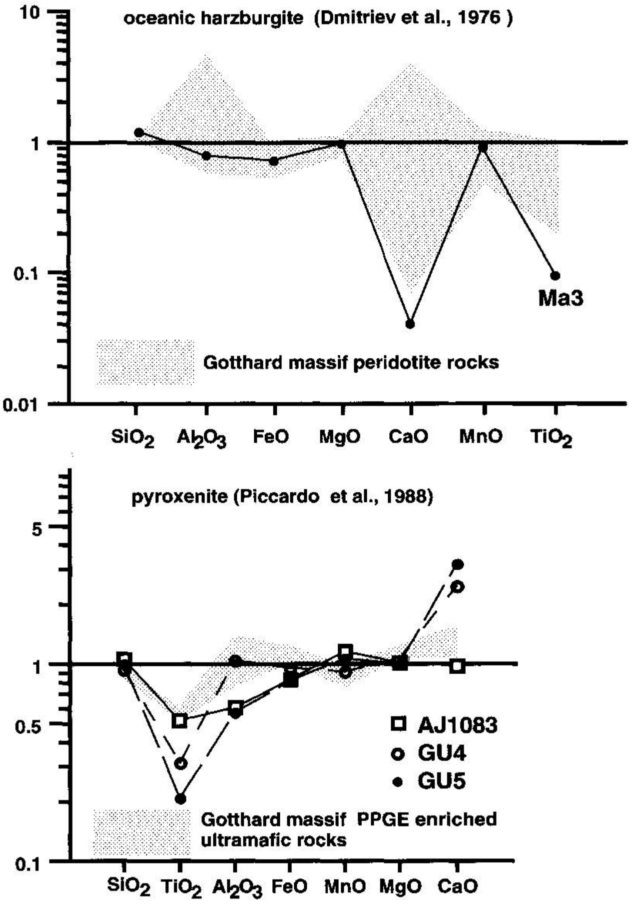

Fig. 4 Abundances of SiO_2–TiO_2–Al_2O_3–FeO–MgO–CaO–MnO in the Aar ultramafic rocks normalized to average oceanic harzburgite estimated by Dmitriev et al. (1976) and to a pyroxenite by Piccardo et al. (1988). The fields represent ultramafic rocks from the Gotthard massif after Biino and Meisel (1993).

The REE concentrations are not related to the present degree of serpentinization expressed as total L.O.I. (Fig. 5), but several cycles of serpentinization and de-serpentinization possibly occurred.

The chondrite-normalised diagrams (data normalised according to Evensen et al., 1978; 1.5 times the original concentration for a volatile free carbonaceous chondrite) are shown in figure 6. Samples AJ1083 and Gu5 show a flat-shaped pattern at chondritic abundances. Sample Gu4 is depleted in LREE. The pattern is possibly comparable to a pattern of a lherzolite. Ma3 is slightly enriched in LREE. Ma3 is not enriched in Ca, Ti, Fe or Al suggesting a decoupling between LREE and major incompatible elements.

The presence of primary amphibole cannot be constrained by petrographic observation, but amphibole-bearing ultramafic rocks usually have high REE abundance (McDonough and Frey, 1989), therefore, the investigated samples were probably anhydrous. The concentration in REE is also lower than that observed in komatiite rocks.

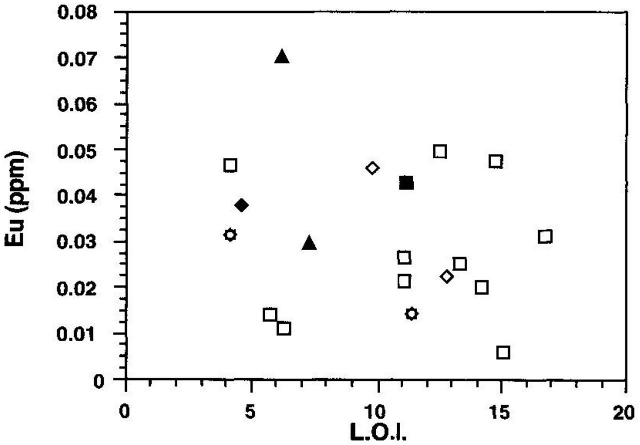

Fig. 5 Eu versus L.O.I.. The degree of alteration (L.O.I.) is not correlated with Eu abundance. Aar massif: ■ Ma3; ▲ Gu4 and Gu5; ◆ AJ1083. Gotthard massif (Biino and Meisel, 1993): □ lherzolite and harzburgite rocks; ◇ enriched peridotite rocks; ✪ cumulite rocks from basaltic melt.

5.4. PLATINUM GROUP ELEMENTS (PGE)

It has become a tradition to show the relative abundances of the PGE and Au in rocks normalized to their abundances in C1 chondrites and plotted in order of decreasing melting point (Naldrett and Duke, 1980). The PGE normalized concentrations are shown in figure 7.

All the investigated samples show a spread in Au concentration. It can be attributed to the mobility during serpentinization, sampling and analytical problems (nugget effect). Gold is uncorrelated to PGE. Similar chemical behaviour has already been observed in several investigations. It may turn out that physico-chemical processes responsible for PGE distribution are not the same as those controlling Au. Therefore, Au is not discussed further.

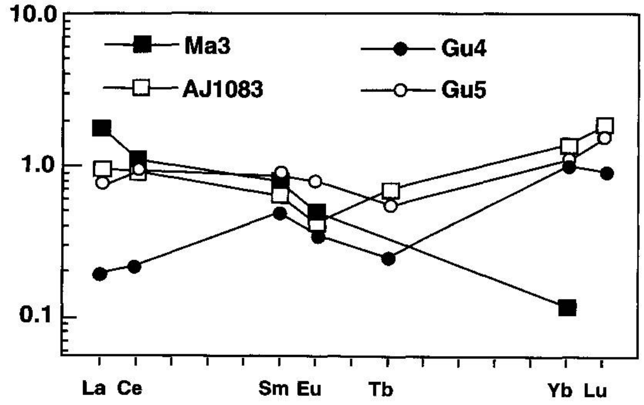

Fig. 6 Chondrite normalized REE abundances of the Aar ultramafic rocks.

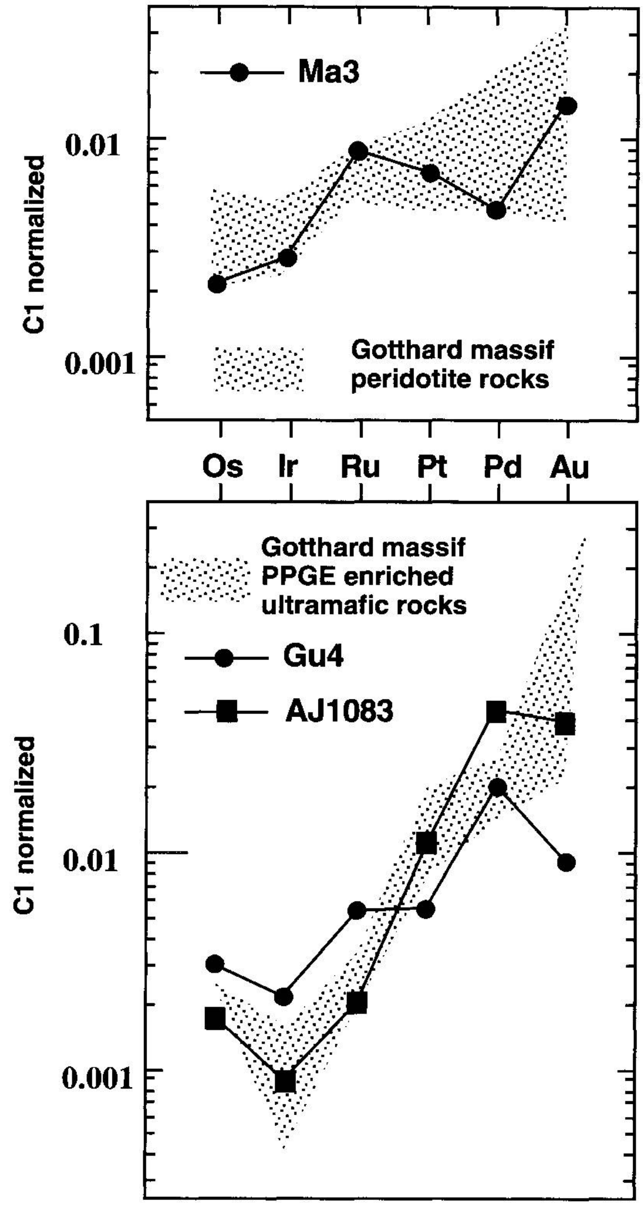

Fig. 7 Chondrite normalized PGE abundances in the Aar ultramafic rocks. C1 normalization values after Naldrett and Duke (1980). The fields represent ultramafic rocks from the Gotthard massif (Biino and Meisel, 1993).

Even though the range of PGE abundances is limited, the previously suggested subdivision in two groups is confirmed by them. The two groups can be separated by the absolute abundance and ratios of IPGE versus PPGE. This discrimination can be expressed by elemental ratios, e.g., Pt/Ir vs Pt. Two samples from the Gotthard massif have been included in the following discussion of group II.

First group: Ma3 has an almost flat to a slight positive slope of the C1 normalized abundance pattern. Comparing the PGE pattern with the lit-

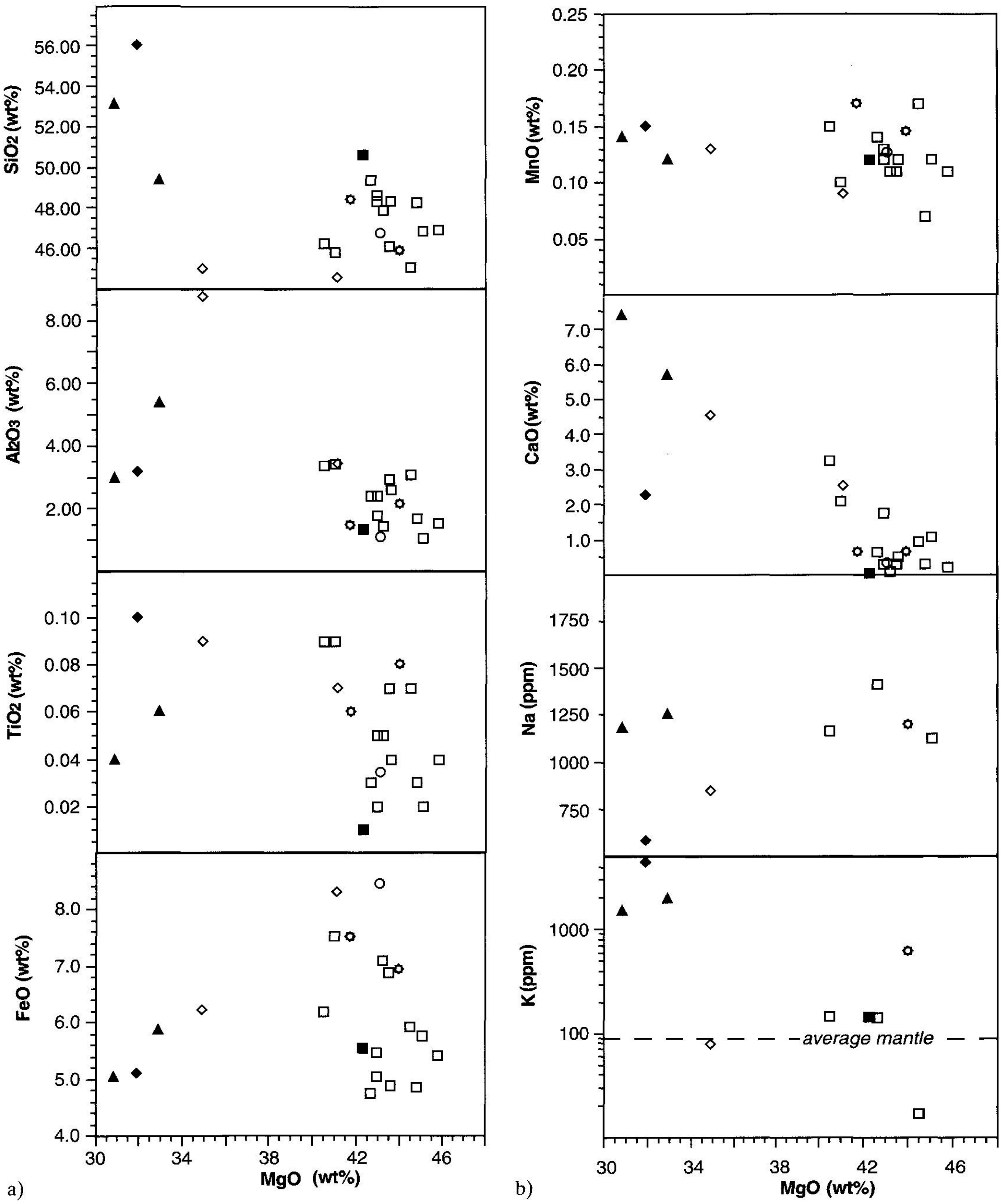

Fig. 8 Major elements variation diagrams in Helvetic ultramafic rocks as a function of MgO (wt%). Aar massif: ■ Ma3; ○ KAW 2076 (Schaltegger, 1984); ▲ Gu4 and Gu5; ◆ AJ1083. Gotthard massif (Biino and Meisel, 1993): □ lherzolite and harzburgite rocks; ◇ enriched peridotite rocks; ✪ cumulite rocks from basaltic melt.

erature, Ma3 shows an affinity with slightly enriched harzburgites.

Second group: has a lower IPGE and a higher PPGE abundance compared to Ma3. They show a very high variability, but a positive correlation exists between Ir/Cr, Ir/Ru, Ir/CaO, and Ru/CaO (also a weak correlation of Cr/CaO, Sc/CaO) thus clinopyroxene formation is correlated with the process controlling the IPGE abundance. The enrichment in the PPGE characterizes these samples. The PPGE enrichment will be discussed in a following section.

5.5. Mg VARIATION DIAGRAMS AND DISCUSSION OF THE CHEMICAL DATA

In the following the chemical composition of the ultramafic rocks of the Aar and Gotthard massifs will be discussed (Figs 8, 9, 10). In the Gotthard massif two geodynamically distinct types of ultramafic rocks were distinguished on geochemical and field grounds (cumulite peridotites from basaltic melt and abyssal peridotites; Biino and Meisel, 1993). In the abyssal peridotites of the Gotthard massif the same subdivision in group one and group two has been made.

The concentration of MgO is a good index for discriminating different ultramafic rock types, but crustal cumulate ultramafic rocks (i.e. samples from the Gotthard massif represented by stars in Figs 8, 9, 10) cannot be discriminated.

Al and Mg behave antithetically during mantle processes. Therefore, a negative trend should be shown by the plot MgO versus Al_2O_3 (Fig. 8). This trend is not clearly shown. It is suggested that during serpentinization MgO and Al_2O_3 behave differently or are mobilized at different degrees. For example, four samples have MgO greater than 44 wt% (transition between lherzolite and harzburgite according to Pfeifer et al., 1993), but eight samples have Al_2O_3 less than 2 wt% (approximate value corresponding to the equivalent transition). Biino and Meisel (1993) observed a correlation between chlorite and Al abundance. Since chlorite is concentrated in monomineralic millimetre-thick shear zones, they concluded that Al concentration is also perturbed by fluid-rock interaction.

Calcium shows a good correlation with MgO, and its mobility cannot be a general process during serpentinization. Iron and Mn show poor correlation with MgO.

The alkali abundances in the ultramafic rocks are extremely low, ruling out important Na- and K-exchange with more alkali-rich country rocks or alkali-mantle metasomatism. The abundance

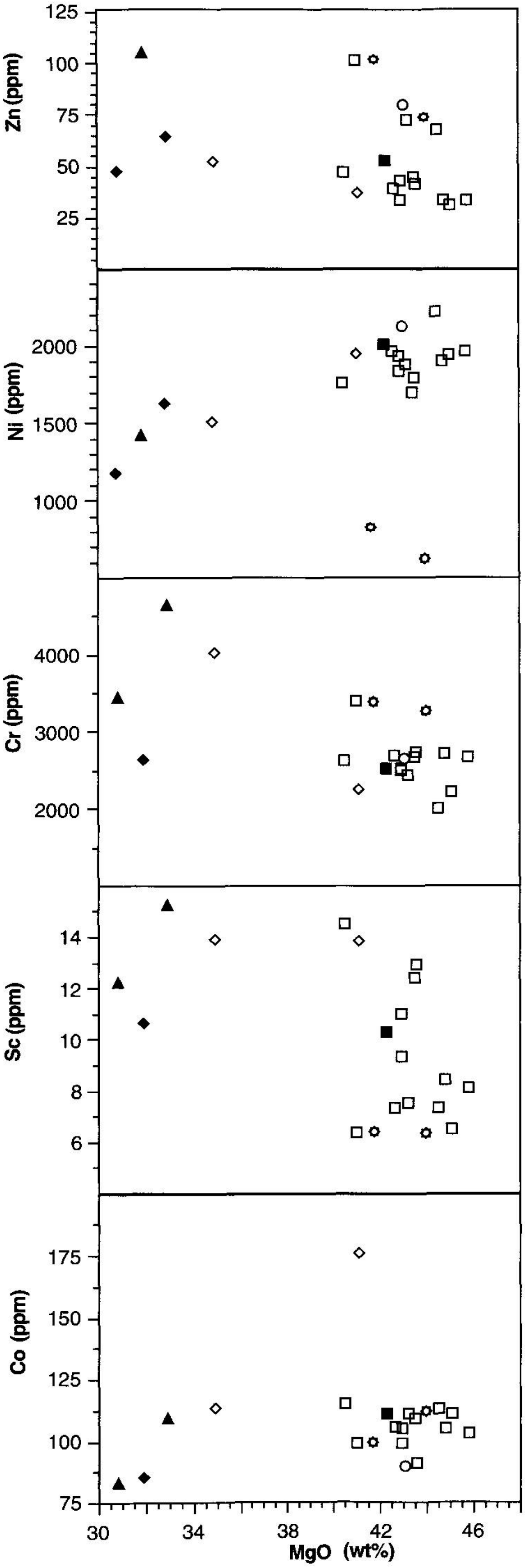

Fig. 9 Trace elements variation diagrams in Helvetic ultramafic rocks as a function of MgO (wt%). Symbols as in figure 8.

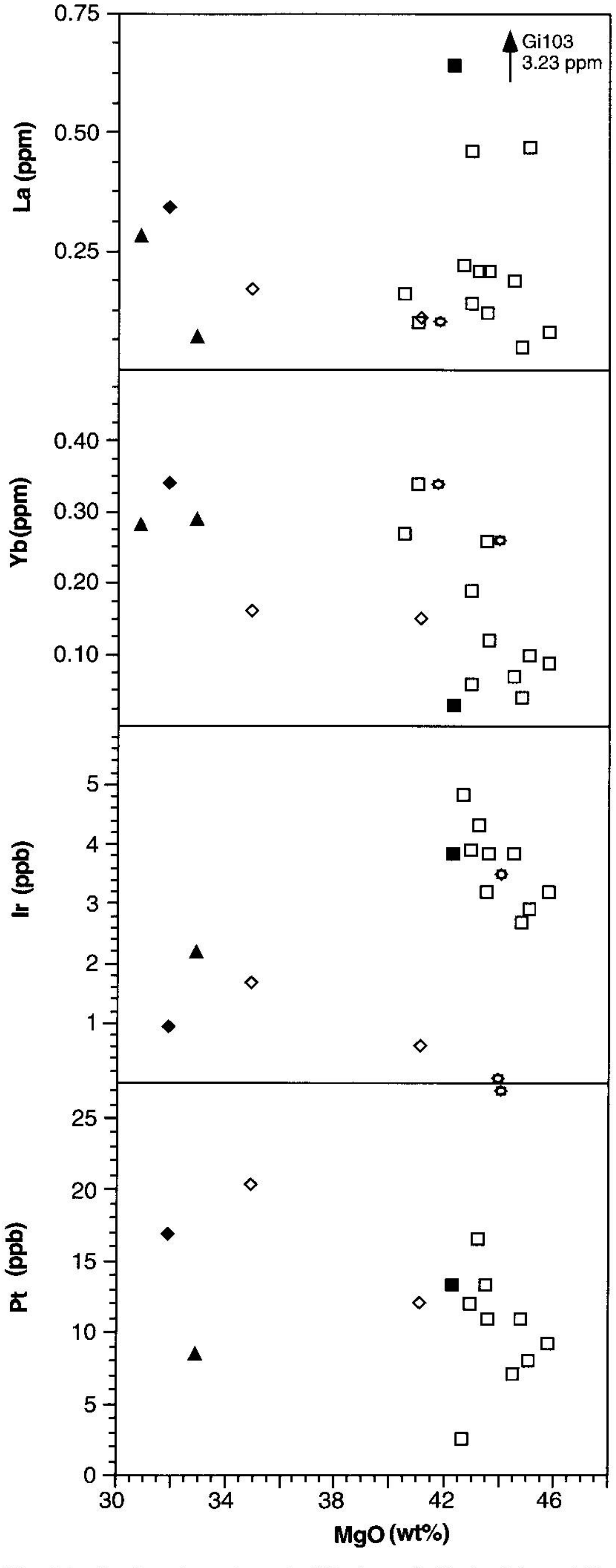

Fig. 10 Lathanium (ppm), Yb (ppm), Ir (ppb) and Pt (ppb) variation diagrams in Helvetic ultramafic rocks as a function of MgO (wt%). Symbols as in figure 8.

of K in the upper mantle is estimated to be about 91 ppm (Azbel and Tolstikhin, 1990), and large parts of the investigated samples show abundances below 100 ppm (detection limit). The samples with higher K_2O have low MgO abundances suggesting a primary fractionation.

In samples from group II there are no correlations between REE and MgO abundances. They do not fit in the trend or field defined by the other samples. It suggests a different genetic and primary evolution mechanism (precipitation from melt as discussed in the following section). The high and restricted range of Mg number suggests that the melts were homogeneous and not extensively differentiated.

It is interesting to remark in passing that there exists a negative trend between Sc (or CaO) and Ni (Fig. 11). Scandium and CaO abundance is controlled by clinopyroxene and Ni abundance by olivine and ores, and the plotted samples lie on a mixing curve between these minerals.

The bulk composition of the ultramafic rocks of the Helvetic basement are remarkably similar, and comparable to that of ultramafic rocks still preserving mantle assemblages. This chemical similarity and several "igneous looking" trends are difficult to account for, if the present compositions are results of extensive metasomatism.

It is traditionally believed that PGE are essentially immobile during serpentinization (Edwards, 1990; Hattori and Hart, 1991; Ohnenstetter, 1992). Since Ir is not mobilized in a wide range of geologic environments its concentration is considered in the following as primary magmatic.

No positive correlation exists between Ir and MgO which would at first sight be expected from Ir incorporation in forsterite. Poor correlation between Ir and Mg were already described (Lee and Tredoux, 1986). There is no significant statistical correlation between Cr and IPGE, which implies that Cr-bearing spinel did not control the fractionation of the IPGE. This result is surprising since Ir^{4+} has an ionic radius of 0.71 Å and the radius of Cr^{3+} is 0.70 Å, but PGE usually made up separate minerals that are texturally associated with spinel (Oshin and Crocket, 1982; Garuti et al., 1984; Prichard et al., 1985). A strong positive correlation between Ir and Ni is observed (correlation coefficient 0.765, n = 12). Thus, sulphides or alloys (and neither olivine nor chromite) are the controlling minerals of the IPGE distribution. The good positive correlation between Ir–Os (Fig. 8) and Ir–Ni is in agreement with the hypothesis of alloys formation. Similar trends are evident for Ru, but the correlation coefficient is poor. The process responsible for

IPGE concentration did not fractionate IPGE. There is no covariance between REE and PGE concentrations as already illustrated by Hamlyn et al. (1985).

Deformation and metamorphism preclude the recognition of komatiites by typical petrographic methods. The chemical composition of the investigated ultramafic rocks is comparable to Archean komatiite peridotites (Lesher, 1989). PGE may offer the best means of characterizing the affinity of the Helvetic ultramafic rock suite. The chondrite-normalized PGE patterns are not similar to the flat pattern typical for Archean komatiite (e.g. Langmuir, Mount Edwards, Kambalda; Naldrett, 1981). Younger komatiite rocks have different composition (MgO < 30 wt%). The evolution trends proposed for the Gorgona Island komatiite basaltic rocks are quite different and are mainly controlled by olivine fractionation (Brügmann et al., 1987).

6. Interpretation of the data

6.1. CRUSTAL METASOMATISM

Before attempting to evaluate the significance of the results it is important to examine the potential effects of crustal metasomatism first.

Fluid-ultramafic rocks reactions may be responsible for the process of silicification of the ultramafic rocks, since the infiltrating fluids have been buffered by quartz. Fluid-rock interaction should be responsible for the high silicon content in Ma3 and AJ1083.

REE mobility during serpentinization is quite controversial. Interaction between H_2O-rich fluid and ultramafic rocks does not affect the REE concentrations, but intense secondary mobilization of REE is described in komatiite percolated by CO_2 (or CH_4)-rich fluids (Tourpin et al., 1991; Gruau et al., 1992). The LREE are transported by CO_2 (or CH_4)-rich fluids and concentrate in the calcite or dolomite precipitating in the ultramafic rocks, and depletion in LREE is described in a magnesite-bearing sample from the Gotthard massif (Biino and Meisel, 1993). The enrichment in LREE observed in sample Ma3 is not correlated to calcite or dolomite precipitation. Therefore, the observed patterns may represent processes which occurred in the mantle or during high temperature oceanic emplacement. It is expected (but was not observed) that during partial melting $(La/Yb)_n$ should decrease with decreasing Ca or other incompatible elements. The observed LREE enrichment can be the result of LREE transport by aqueous fluids occurring in sub-continental but also in sub-oceanic mantle or by oceanic refertilization due to melt percolation.

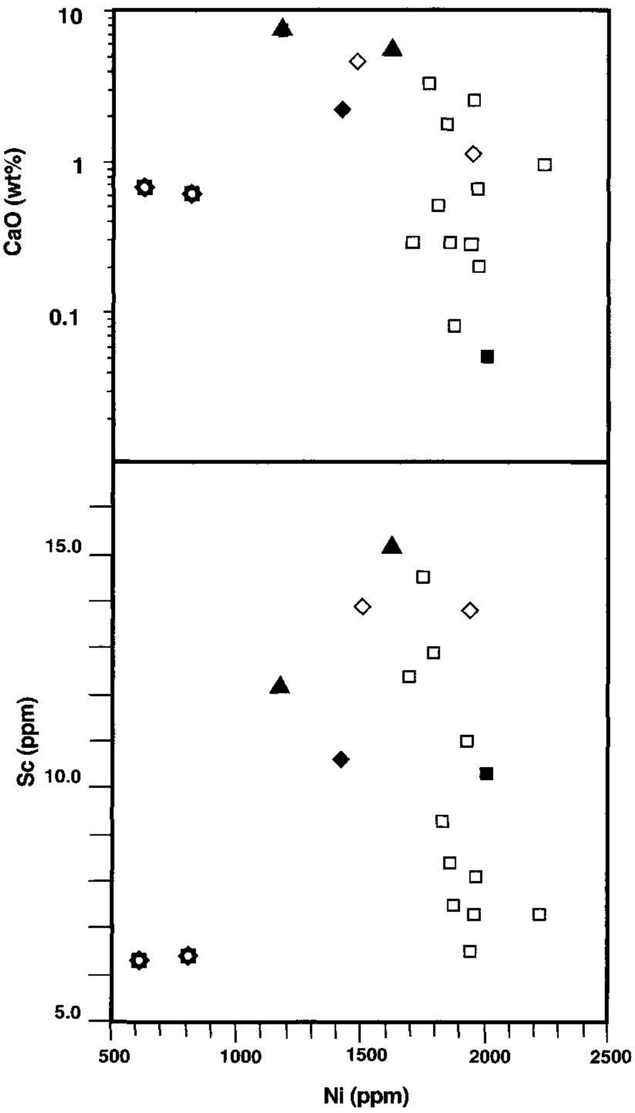

Fig. 11 CaO (wt%) and Sc (ppm) versus Ni (ppm). Symbols as in figure 8. The trend possibly represent a mixing curve between Cpx and Ol components.

Barnes et al. (1985) suggested that PPGE are depleted in komatiite that have undergone talc-carbonate alteration. Our investigation suggest that their conclusion cannot be generalized to all the ultramafic rocks showing talc-carbonate alteration. Several recent studies (Wood, 1987; Wood et al., 1989; Wood and Mountain, 1991; Wood et al., 1992; Gammons et al., 1992) showed that PGE solubilities in fluid decrease with decreasing f_{O_2} and increase with both temperature and pH, and sea water interaction is not responsible for important PGE leaching (Anbar et al., 1992). Therefore serpentinization is not a process responsible for PGE mobilization, and PGE abun-

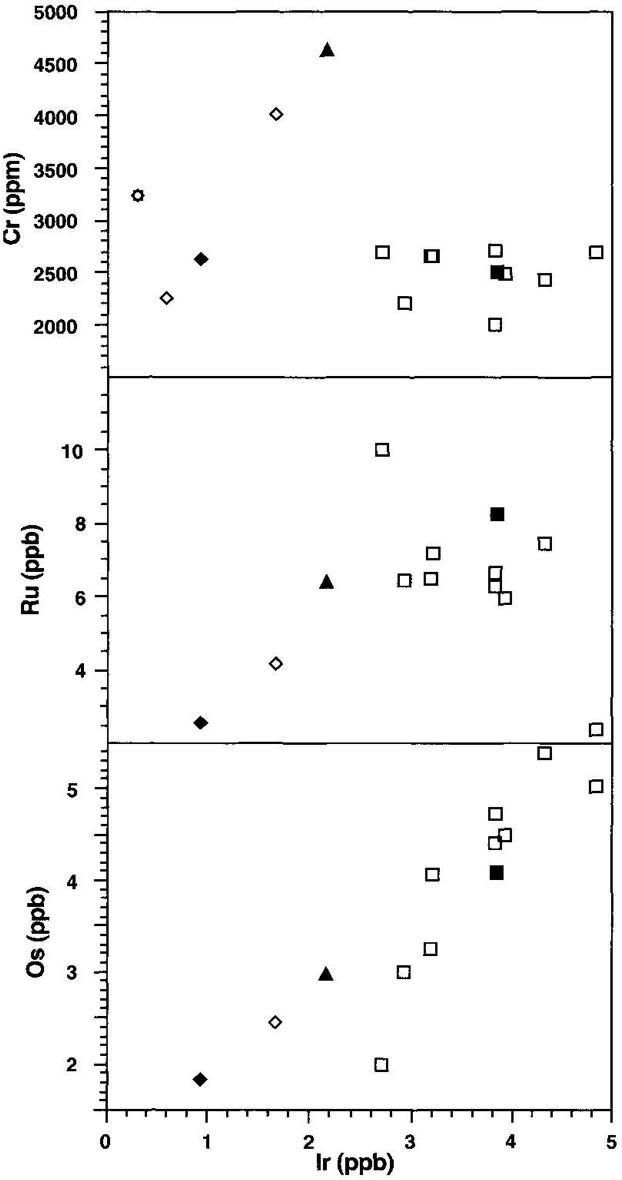

Fig. 12 Cr (ppm), Ru (ppb), Os (ppb) versus Ir (ppb). Aar massif: ■ Ma3; ▲ Gu4 ; ◆ AJ1083. Gotthard massif (Biino and Meisel, 1993): □ lherzolite and harzburgite rocks; ◇ enriched peridotite rocks; ✪ cumulite rocks from basaltic melt. Cr versus Ir diagram evidences the different evolution trends of the two ultramafic groups.

dances should be useful tools to determine the magmatic petrogenesis of the ultramafic rocks.

6.2. THE IMPREGNATION IN THE MANTLE

Nevertheless, the investigated samples show a peculiar chemical composition. The major, trace and RE elements show a partial depletion of the ultramafic rocks and minor crustal metasomatism, but PGE data are compatible with enriched ultramafic rocks. These patterns suggest that processes other than partial melting or alteration affected the chemical composition of the ultramafic rocks. A partial melting process leads to an enriched magma with PPGE > IPGE and a residual mantle characterized by a flat to negative PGE pattern (PPGE ≤ IPGE; IPGE are poorly soluble in basaltic melt whereas PPGE are compatible). Magmatic processes such a fractionated melt infiltration in harzburgitic sequences may be responsible for refertilization of peridotites.

Edwards (1990) encountered the same puzzle in the Bay of Islands Ophiolite Complex. He explained the enriched harzburgites by addition of a few percent of an orthopyroxenitic component with Pd/Ir ratios over 50 to a depleted residual harzburgite with a low Pd/Ir ratio of 0.21.

In this case, the investigated rocks were probably a residue from partial melting (group I; depletion of PPGE) and precipitated from melt (group II; depletion of IPGE). It is suggested that IPGE are removed early from the melt by laurite or IPGE-bearing alloys, but PPGE are mostly retained by the melt. Oshin and Crocket (1982) have suggested that an evolving magma becomes enriched in PPGE if sulfur saturation is not reached. Therefore, crystallization of the melt produces rocks that are IPGE depleted. Later on, both rock types have been refertilized at different degrees by a percolating basaltic melt. Sulfur may have reached saturation during fractionation of the basaltic melt, PPGE-mineral phases precipitate from the melt and a refertilization of the ultramafic rocks occurred. MORB-type basalts are sulfur saturated at the time of extrusion. Several authors suggest that MORB-type basalts may also be S-saturated already in the mantle and that a sulphide component remains in the mantle (Jagoutz et al., 1979; Morgan et al., 1981; Garuti et al., 1984; Hamlyn et al., 1985), since PGE-bearing sulphides are commonly described in peridotites (e.g. Garuti et al., 1984; Fig. 22, pag. 81). In the rock studied the role of S (and sulphide formation) as a controlling factor in IPGE is not clear, and alteration can obscure the abundance. Tentatively, here Ni–Fe alloys are the primary IPGE-bearing phases. Bird and Basset (1980) suggested that IPGE-alloys play a significant role in mantle PGE geochemistry, but this idea has not been carefully evaluated. Prichard et al. (1985) described IPGE alloy in chromite. In these cases, sulfur fugacities of ultramafic rocks are probably low enough for the alloy rather than Ir–Os sulphide, to be stable.

A refertilization process is described at the transition zone between mantle and oceanic crust (Edwards, 1990; Ohnenstetter, 1992). Impregnation in mantle rocks reflects magmatism in oce-

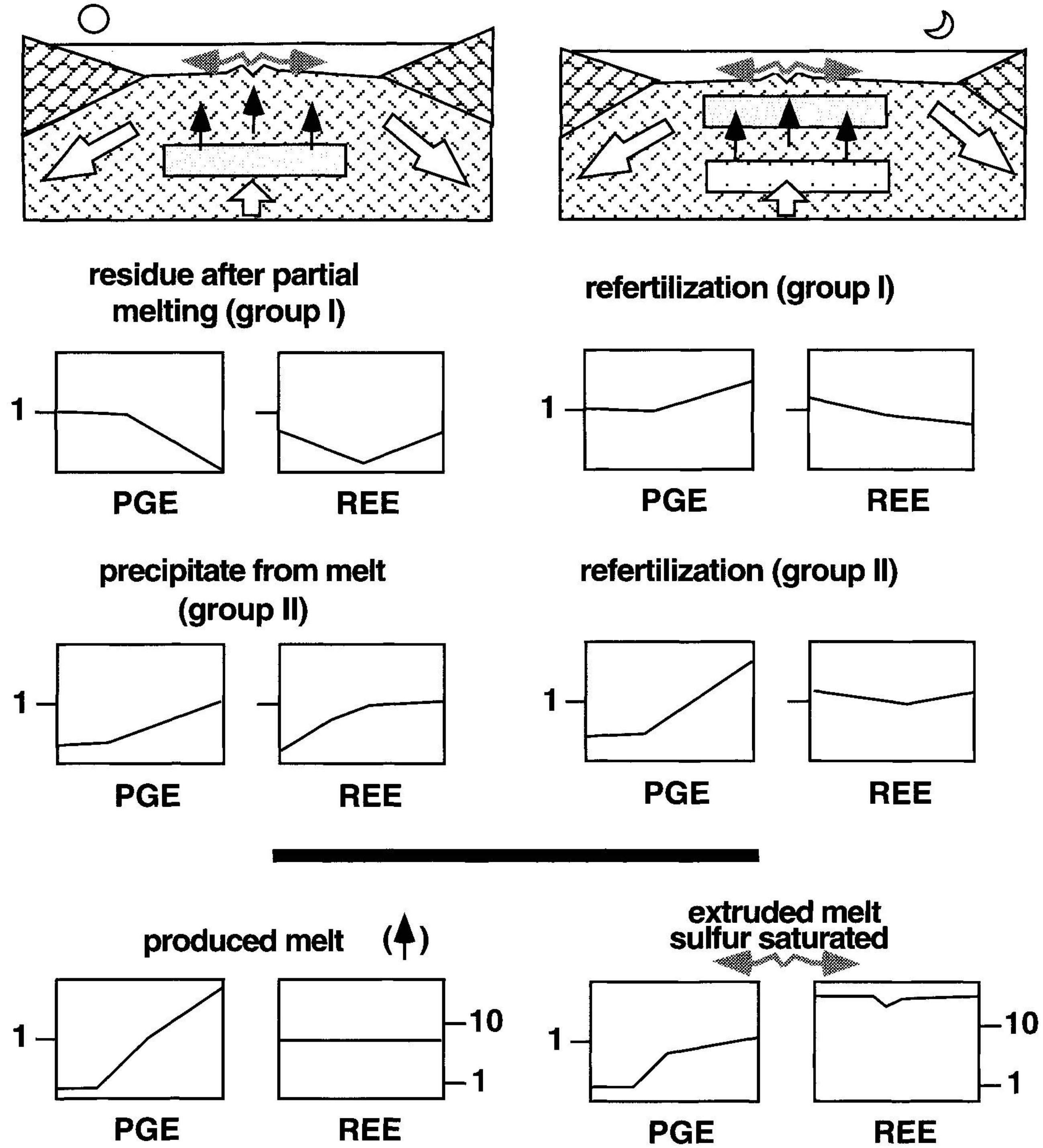

Fig. 13 Two cross sections through the hypothetical pre-Caledonian ocean. The first cross section represents the stage when the Helvetic ultramafics were partially or totally molten. The second cross section represent a further in time stage corresponding to the time when the ultramafics were at a higher structural level and were infiltrated by melts produced further down. Partial melting is responsible for PPGE depletion. Crystallization from melt produces a IPGE depleted rock with a possible positive PPGE slope. Infiltration of basaltic melt is responsible for PPGE enrichment. The PGE concentration of the extruded melt is after the point at which the melt becomes saturated in sulfide.

anic basins (Nicolas and Prinzhofer, 1983; Nicolas and Dupuy, 1984; Toramaru and Fujii, 1986; Navon and Stolper, 1987; Nicolas, 1989; Kelemen et al., 1992; Elthon, 1992; Ohnenstetter, 1992) or K-metasomatism in the sub-continental mantle (McKenzie, 1989). The impregnation process is still a matter of disputation. The px-rich peridotites and pyroxenites are considered to reflect pathways for migration of mantle melts. Their petrogenesis is controversial and may be produced either by (i) mingling of melt and mantle xenocrysts (NICOLAS, 1986; KELEMEN et al., 1992), (ii) early crystallization products of picritic magmas (SMEWING, 1981), (iii) cumulates from Al-poor magmas (ELTHON et al., 1984). Complex superposition of several mechanisms such as melt-rock reaction, trapping of melt, and filter pressing may also be responsible for enrichment. The PPGE enriched samples (e.g. Gu4 and Gu5) represent layered rocks, but from field observation it is difficult to decide which of the possible mechanisms controlled the refertilization.

Due to mantle impregnation, chemical elements do not necessarily correlate with the degree of partial melting as suggested by several studies, but a more complicated evolution has to be taken into account. The simplest petrologic model for these ultramafic rocks is that they are made up by two components. A first component is a peridotite mantle depleted to various degrees, and the second is represented by an infiltrating basaltic melt. The basaltic component is responsible for the PGE (± LREE) enrichment and compatible elements decoupling. A very strong correlation between Os isotope ratio and Sc or Co abundances observed in the rocks studied (as Ni versus Sc correlation) is supporting the impregnation model.

The transitional element abundances are good markers of solid-liquid reaction (both partial melting and contamination) since they have a very high partition coefficient. Therefore, large diversity of the REE and PPGE patterns is also expected for products derived from partial melting, melt infiltration, and cumulus processes. It turns out that the Ni/Co ratio seems to be a useful and easy tool to discriminate the mantle ultramafic rocks from the ultramafic rocks cumulated from a basaltic melt. Peridotites, that underwent a certain degree of reaction with basaltic melt, show a decrease in the Ni/Co ratio. This ratio may be used in order to trace the infiltration process also without PGE analysis.

7. Comparison to other ultramafic rocks in the Central Alps

The characterization of the mafic-ultramafic rocks of the Aar massif is still sketchy. The pervasive retrogression and the later migmatitic event makes it difficult to investigate a larger number of localities. Nevertheless, chemical comparison between the ultramafic rocks occurring in the Aar massif and that of the Gotthard massif is probably according to the presented data. Ma3 and sample KAW 2076 from the Sustenpass (SCHALTEGGER, 1984) are comparable to the abyssal peridotites of the Gotthard massif (BIINO and MEISEL, 1993). The field association of the ultramafic rocks with MORB suggests a mantle uplift in an oceanic basin of the ultramafic rocks of the Helvetic basement. The presence of chromite constrains a primary lithospheric emplacement at the transition zone between crust and mantle in harzburgite ophiolite type sequence (NICOLAS, 1989). The ultramafic rocks cropping out in the Gotthard massif were interpreted as remnants of an oceanic sequence tectonically emplaced in an accretionary wedge of pre-Caledonian age (ABRECHT et al., 1991; BIINO and MEISEL, 1993; PFEIFER et al., 1993). Indeed, the ultramafic rocks of the Aar massif may also be considered oceanic rocks emplaced in an active margin sequence.

In the Central Alps the association of ultramafic rocks with mafic rocks and paragneiss is also striking (PFEIFER et al., 1993), and evidence for a back arc basin evolution is not described. Therefore, the accretionary wedge model proposed for the Helvetic basement may be valid at a regional scale.

8. Conclusions and geological consequences

One obvious way to understand the Earth's upper mantle petrogenesis is to study the mantle ultramafic rocks that are brought to the orogenic terranes by tectonics. Unluckily, several petrogenetic processes occurring in the upper mantle are beyond study because of serpentinization. Nevertheless, by comparison of different chemical elements, it is possible to decipher the chemical evolution of the serpentinized ultramafic rocks.

Serpentinization and magmatic impregnation are the two distinct metasomatic processes evident in the ultramafic rocks of the Helvetic basement. The scale of element mobility during serpentinization cannot be generalized, as several few elements show mobility and only PGE, Ni, Co and Sc are immobile. REE and other elements (e.g. Ca) were probably not affected (or only slightly affected) by serpentinization. Iron, Mn and in few samples Al were mobilized at different degree. Samples of group II show a good correlation between Ir and Ca which suggests that Ca can be immobile under certain conditions. The possibility of hydrothermal leaching, transport and precipitation of PGE is ruled out because all the possible conditions for higher PGE mobility (oxidation, low pH) are unrealistic during serpentinization. A mantle refertilization produced by melt impregnation is proposed in order to explain PGE distribution patterns of the ultramafic rocks.

The ultramafic rocks from the Helvetic basement are clearly mantle derived rocks. Sub-oceanic- and sub-continental- mantle ultramafic rocks show in first approximation comparable major element distribution (DMITRIEV et al., 1976; MAALØE and AOKI, 1977). The major element compositions are compatible with any of several possible protoliths for mantle ultramafic rocks and place no strong constraints on their ultimate origin. Highly depleted peridotites were not observed, therefore, a genesis along an active margin is excluded (BONATTI and MICHAEL, 1989).

Secondary enrichments in PPGE (± LREE) are typical of sub-oceanic peridotites. The refertilization process is attributed to basalt-ultramafic rock reaction during basaltic melt uprising under an oceanic ridge. The sequence of events responsible for the observed chemical composition are summarised in a schematic cartoon (Fig. 13).

ABRECHT et al. (1991) suggested that the ultramafic rocks are relics of an oceanic plate accreted into an active margin. This proposed tectonic scenario seems to be consistent with the geochemical signature observed in this work. The partial enriched nature of samples studied must reflect a relic of oceanic ridge processes.

The general scheme proposed by NICOLAS and JACKSON (1972; i.e. continental region underlain by undepleted mantle and oceanic basins by depleted mantle), requires revision. BOUDIER and NICOLAS (1985) proposed that harzburgites are the result of fast spreading and lherzolite the result of low spreading. In our view, the spreading rate may reflect not only the degree of melting, but also the degree of refertilization. Sub-oceanic mantle heterogeneity was already suggested by BOWEN (1927) and confirmed by recent research (e..g. BONATTI et al., 1992). The possibility to correlate this heterogeneity (for example expressed as degree of depletion by MgO, Al_2O_3, FeO or CaO abundances) to geodynamic environments may lead to erroneous conclusions, because the chemical composition observed within the oceanic lithosphere may also be influenced by the interaction of a depleted lithosphere with percolating basaltic melts.

A complete geochemical investigation is necessary in order to trace back to earlier petrogenetic stages of this poly-metamorphic rocks, and platinum group elements can provide an unique input into the understanding of the genetic processes.

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References

ABRECHT, J. (1980): Zur Bildung migmatitischer Schollenamphibolite aus dem Altkristallin des Aarmassivs. Geol. Rundsch. 69, 695–725.

ABRECHT, J. (1994): Geological units of the Aar massif and their pre-Alpine rock associations: A critical review. Schweiz. Mineral. Petrogr. Mitt. 74, 3–25.

ABRECHT, J., BIINO, G.G., MERCOLLI, I. and STILLE, P. (1991): Mafic-ultramafic rock associations in the Aar, Gotthard and Tavetsch massifs of the Helvetic domain in Central Swiss Alps: markers of ophiolitic pre-Variscan sutures, reworked by polymetamorphic events? Schweiz. Mineral. Petrogr. Mitt. 71, 295–300.

ABRECHT, J. and SCHALTEGGER, U. (1988): Aplitic intrusions in the Central Aar massif basement: geology, petrography and Rb/Sr data. Eclogae geol. Helv. 81, 277–239.

ANBAR, D.A., CREASER, R.A., PAPANASTASSIOU, D.A. and WASSERBURG, G.J. (1992): Rhenium in seawater: confirmation of generally conservative behaviour. Geochim. Cosmochim. Acta 56, 4099–4103.

AZBEL, I.YA. and TOLSTIKHIN, I.N. (1990): Geodynamic, magmatism, and degassing of the Earth. Geochim. Cosmochim. Acta 54, 139–154.

BARNES, S.-J., NALDRETT, A.J. and GORTON, M.P. (1985): The origin of the fractionation of platinum-group elements in terrestrial magmas. Chem. Geol. 53, 303–323.

BIINO, G.G. and MEISEL, T. (1993): Geochemistry of polymetamorphic ultramafics (major, trace, noble and rare earth elements): an example from the Helvetic basement (Central Alps, Switzerland). Mineralogy and Petrology, 49, 189–212.

BIRD, J.M. and BASSET, A. (1980): Evidence of a deep mantle history in terrestrial osmium-iridium-ruthenium alloys. J. Geophys. Res. 85, 5461–5470.

BONATTI, E. and MICHAEL, P.J. (1989): Mantle peridotite from continental rift to ocean basins to subduction zones. Earth Planet. Sci. Lett. 91, 297–311.

BONATTI, E., PEYVE, A., KEPEZHINSKAS, P., KURENTSOVA, N., SEYLER, M. and UDINTSEV, G. (1992): Upper mantle heterogeneity below the Mid-Atlantic Ridge, 0–15° N. J. Geophys. Res. 97, 4461–4476.

BOUDIER, F. and NICOLAS, A. (1985): Harzburgite and lherzolite subtypes in ophiolitic and oceanic environments. Earth Planet. Sci. Lett. 76, 84–92.

BOWEN, N.L. (1927): The evolution of Igneous rocks. Princeton Univ. press, 323 pp.

BRÜGMANN, G.E., ARNDT, N.T., HOFMANN, W.A. and TOBSCHALL, H.J. (1987): Noble metal abundances in komatiite suites from Alexo, Ontario, and Gorgona Island, Colombia. Geochim. Cosmochim. Acta 51, 2159–2169.

CURRIE, L.A. (1968): Limits for quantitative detection and qualitative determination: application to radiochemistry. Analyt. Chem., 40, 586–593.

DMITRIEV, L.V., UKHANOV, A.V. and SHARASKIN, A.Y. (1976): Petrochemical types of mantle peridotites. Geochim. Int. 13, 122–127.

Edwards, S.J. (1990): Harzburgites and refractory melts in the Lewis Hills massif, Bay of Islands ophiolite complex: the base-metals and precious-metals story. Can. Mineral. 28, 537–552.

Elthon, D. (1992): Chemical trends in abyssal peridotites: refertilization of depleted suboceanic mantle. J. Geophys. Res. 97, 9015–9025.

Elthon, D., Casey, J.F. and Komor, S. (1984): Cryptic mineral-chemistry variations in a detailed traverse through the cumulate ultramafic rocks of the North Arm mountain massif of the Bay of Islands ophiolite, Newfoudland. In : I.G. Gass, S.J. Lippard and A.W. Shelthon (eds): Ophiolite and oceanic lithosphere. London, Geological Society, 83–97.

Evensen, N.W., Hamilton, P.J. and O`Nions, R.K. (1978): Rarc-carth abundances in chondritic meteorites. Geochim. Cosmochim. Acta 42, 1199–1213.

Frey, F.A. (1984): Rare earth element abundances in upper mantle rocks. In: Henderson, P. (ed.): Rare earth element geochemistry. Elsevier Amsterdam, 153–203.

Frey, F.A. and Prinz, M. (1978): Ultramafic inclusion from San Carlos, Arizona: petrologic and geochemical data bearing on their petrogenesis. Earth Planet. Sci. Lett. 38, 129–176.

Frey, F.A., Suen, C.J. and Stockman, H.W. (1985): The Ronda high temperature peridotite: geochemistry and petrogenesis. Geochim. Cosmochim. Acta 49, 2469–2491.

Frey, M., Bucher, K. and Mullis, J. (1980): Alpine metamorphism along the Geotraverse Basel–Chiasso – a review. Eclogae geol. Helv. 73, 527–546.

Gammons, C.H., Bloom, M.S. and Yu, Y. (1992): Experimental investigation of the hydrothermal geochemistry of platinum and palladium: I. Solubility of platinum and palladium sulfide minerals in NaCl/ H_2SO_4 solutions at 300 °C. Geochim. Cosmochim. Acta 56, 3881–3894.

Garuti, G., Gorgoni, C. and Sighinolfi, G.P. (1984): Sulfide mineralogy and siderophile element abundances in the Ivrea-Verbano mantle peridotites (Western Italian Alps). Earth Planet. Sci. Lett. 70, 69–87.

Gruau, G., Tourpin, S., Fourcade, S. and Blais, S. (1992): Loss of isotopic (Nd, O) and chemical (REE) memory during metamorphism of komatiites: new evidence from eastern Finland. Contrib. Mineral. Petrol. 112, 66–82.

Hamlyn, P.R., Keays, R.R., Cameron, W.E., Crawford, A.J. and Waldron, H.M. (1985): Precious metals in magnesian low-Ti lavas: implications for metallogenesis and sulfur saturation in primary magmas. Geochim. Cosmochim. Acta 49, 1797–1811.

Hart, S.T. (1988): Heterogeneous mantle domains: signatures, genesis and mixing chronologies. Earth Planet. Sci. Lett. 90, 273–296.

Hattori, K. and Hart, S.R. (1991): Osmium-isotope ratios of platinum-group minerals associated with ultramafic intrusions Os-isotopic evolution of the oceanic mantle. Earth Planet. Sci. Lett. 107, 499–514.

Jagoutz, E., Baddenhausen, H., Blum, K., Cenfales, M., Dreibus, G., Spettel, B., Lorenz, V. and Wänke, H. (1979): The abundances of major, minor and trace elements in the earth's mantle as derived from primitive ultramafic nodules. Proc. Lunar. Planet. Sci. Conf. 10th, 2031–2050.

Kelemen, P.B., Dick, H.J.B. and Quick, J.E. (1992): Formation of harzburgite by pervasive melt/rock reaction in the upper mantle. Nature 358, 635–641.

Kurat, G., Palme, H., Spettel, B., Baddenhausen, H., Hofmeister, H., Palme, C. and Wänke, H. (1980): Geochemistry of ultramafic xenoliths from Kapfenstein, Austria: evidence for a variety of upper mantle processes. Geochim. Cosmochim. Acta 44, 45–60.

Labhart, T.P. (1965): Petrographische Untersuchungen am Südrand des Aarmassivs. Beitr. geol. Karte Schweiz N.F. 124. Lfg.

Lee, C.A. and Tredoux, M. (1986): Platinum group elements abundances in the Lower and Lower Critical Zones of the eastern Bushveld Complex. Econ. Geol. 81, 1087–1095.

Lesher, C.M. (1989): Komatiite-associated nickel sulfide deposits. Ore deposition associated with magmas. In: J.A. Whitney and A.J. Naldrett (eds): Ore deposits associated with magmas. The Economic Geology Publ. Comp. El Paso, 45–101.

Maaløe, S. and Aoki, K. (1977): The major element composition of the upper mantle estimated from the composition of lherzolite. Contrib. Mineral. Petrol. 63, 161–173.

McDonough, W.F. and Frey, F.A. (1989): Rare earth elements in upper mantle rocks. In: Lipin, B.R. and McKay, G.A. (eds): Geochemistry and mineralogy of rare earth elements. Mineralogical Society of America Washington D.C., 21, 99–145.

McKenzie, D. (1989): Some remarks on the movement of small melt fractions in the mantle. Earth Planet. Sci. Lett., 95, 53–72.

Mercolli, I., Biino, G.G. and Abrecht, J. (1994): The lithostratigraphy of the pre-Mesozoic basement of the Gotthard massif: a review. Schweiz. Mineral. Petrogr. Mitt. 74, 27–38.

Morgan, J.W., Wandless, G.A., Petrie, R.K. and Irving, A.J. (1981): Composition of the earth´s upper mantle – I. Siderophile trace elements in ultramafic nodules. Tectonophysics 75, 47–67.

Naldrett, A.J. (1981): Nickel sulfide deposits: classification, composition, and genesis. Econ. Geol. 75th Anniversary Volume, 628–685.

Naldrett, A.J. and Duke, J.M. (1980): Platinum metals in magmatic sulfide ores. Science 208, 1417–1424.

Navon, O. and Stolper, E. (1987): Geochemical consequences of melt percolation: the upper mantle as a chromatographic column. J. Geol. 95, 285–307.

Nicolas, A. (1986): A melt extraction model based on structural studies in mantle peridotites. J. Petrology 27, 999–1022.

Nicolas, A. (1989): Structures of ophiolites and dynamics of oceanic lithosphere. Kluwer, Dordrecht, 367 pp.

Nicolas, A. and Jackson, E.D. (1972): Répartition en deux provinces des péridotites des chaînes alpines logeant la Méditerranée: implications géotectoniques. Schweiz. Mineral. Petrogr. Mitt. 52, 479–495.

Nicolas, A. and Dupuy, C. (1984): Origin of ophiolitic and oceanic lherzolites. Tectonophysics 110, 177–187.

Nicolas, A. and Prinzhofer, A. (1987): Cumulative or residual origin for the transition zone in ophiolites: structural evidence. J. Petrology 24, 188–206.

Niggli, E. (1970): Alpine Metamorphose und alpine Gebirgsbildung. Fortschr. Mineral. 47, 16–26.

Niggli, E. and Niggli, C.R. (1965): Karten der Verbreitung einiger Mineralien der alpidischen Metamorphose in den Schweizer Alpen (Stilpnomelan, Alkali-Amphibol, Chloritoid, Staurolith, Disthen, Sillimanit). Eclogae geol. Helv. 58, 335–368.

Nisbet, E.G., Dietrich, V. and Esenwein, A. (1979): Routine trace element determination in silicate minerals and rocks by X-ray fluorescence. Fortschr. Mineral. 57, 290–293.

OHNENSTETTER, M. (1992): Platinum group element enrichment in the upper mantle peridotites of the Monte Maggiore Ophiolitic Massif (Corsica, France) – Mineralogical evidence for ore-fluid metasomatism. Mineralogy and Petrology 46, 85–107.

OSHIN, I.O. and CROCKET, J.H. (1982): Noble metals in Thetford Mines ophiolites, Quebec, Canada. Part I: Distribution of gold, iridium, platinum, and palladium in the ultramafic and gabbroic rocks. Econ. Geol. 77, 1556–1570.

PFEIFER, H.R., BIINO, G.G., MÉNOT, R.P. and STILLE, P. (1993): Ultramafic rocks in the pre-Mesozoic basement of the Central and External Western Alps. In: VON RAUMER, J. and NEUBAUER, F. (eds): Pre-Mesozoic basement in the Alps. Springer Verlag Berlin, 119–143.

PFLUGSHAUPT, P. (1927): Beiträge zur Petrographie des östlichen Aarmassivs. Schweiz. Mineral. Petrogr. Mitt. 7, 321–378.

PICCARDO, G.B., MESSIGA, B. and VANNUCCI, R. (1988): The Zabargad peridotite-pyroxenite association: petrological constraints on its evolution. Tectonophysics 150, 135–162.

POTTS, P.J., GOWING, C.J.B. and GOVINDARAJU, K. (1992): Preparation, homogeneity evaluation and cooperative study of two new chromitite reference samples CHR-Pt+ and CHR-Bkg. Geostandards Newsletter 16, 81–108.

PRICHARD, H.M., POTTS, P.J., and NEAREY, C.R. (1985): Platinum-group minerals in ophiolite complexes: An example from Shetland. Can. Mineral., 23, 311.

RINGWOOD, A.E. (1979): Origin of the Earth and Moon. Springer Verlag, Berlin, 618 pp.

ROBÉRT, R.V.D., VAN WYK, E. and PALMER, R. (1971): Concentration of the noble metals by a fire-assay technique using nickel sulphide as the collector. National Institute for Metallurgy, NIM South Africa, 14 pp.

REUSSER, C.E. (1987): Phasenbeziehungen im Tonalit der Bergeller Intrusion. Ph. D. Thesis ETH Zürich, pp. 220.

SCHALTEGGER, U. (1984): Geologie und Petrographie der Gneiszone von Erstfeld, Aarmassiv. Uni. Bern.

SCHALTEGGER, U. (1993): The evolution of the polymetamorphic basement in the Central Alps unravelled by precise U–Pb zircon dating. Contrib. Mineral. Petrol. 113, 466–478.

SCHENKER, F. and ABRECHT, J. (1987): Prä-aargranitische Anatexis, variszische Kontaktmetamorphose und alpidische Regionalmetamorphose im Oberhasli (zentrales Aarmassiv, Schweiz). Schweiz. Mineral. Petrogr. Mitt. 67, 13–26.

SMEWING, J.D., CHRISTIANSEN, N.I., BARTHOLOMEW, I.D. and BROWING, P. (1984): The structure of the oceanic upper mantle and lower crust as deduced from the northern section of the Oman ophiolite. In: GASS, I.G., LIPPARD, S.J. and SHELTHON, A.W. (eds): Ophiolite and oceanic lithosphere. London, Geological Society, 41–53.

STECK, A. (1965): Petrographische und tektonische Untersuchungen am Zentralen Aaregranit und seinen altkristallinen Hüllgesteinen im westlichen Aarmassiv im Gebiet Belalp-Grisighorn. Beitr. geol. Karte Schweiz N.F.. 130. Lfg.

STERN, W.B. (1972): Zur röntgenspektrometrischen Analyse von silikatischen Gesteinen und Mineralien. Schweiz. Mineral. Petrogr. Mitt. 52, 1–25.

TORAMARU, A. and FUJII, N. (1986): Convectivity of melt phase in a partially molten peridotite. J. Geophys. Res. 91, 9239–9252.

TOURPIN, S., GRAU, G., BLAIS, S. and FOURCADE, S. (1991): Resetting of REE, and Nd and Sr isotopes during carbonitization of a komatiite flow from Finland. Chem. Geol. 90, 15–29.

VON RAUMER, J., MÉNOT, R.P., ABRECHT, J. and BIINO, G.G. (1993): The pre-Alpine evolution of the External Massifs. In: VON RAUMER, J. and NEUBAUER, F. (eds): Pre-Mesozoic basement in the Alps. Springer Verlag, Berlin, 221–240.

WOOD, S.A. (1987): Thermodynamic calculations of the volatility of the platinum group elements (PGE): the PGE content of fluids at magmatic temperatures. Geochim. Cosmochim. Acta 51, 3041–3050.

WOOD, S.A., MOUNTAIN, B.V. and FENLON, B.J. (1989): Thermodynamic constraints on the solubility of platinum and palladium in hydrothermal solutions: Reassessment of hydroxide, bisulfide and ammonia complexing. Econ. Geol. 84, 2020–2028.

WOOD, S.A. and MOUNTAIN, B.V. (1991): Hydrothermal solubility of palladium in chloride solutions from 300 ° to 700 °C: preliminary experimental results – a discussion. Econ. Geol. 86, 1562–1563.

WOOD, S.A., MOUNTAIN, B.V. and PAN, P. (1992): The aqueous geochemistry of platinum, palladium and gold: recent experimental constraints and a re-evaluation of theoretical predictions. Can. Mineral. 30, 955–982.

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