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NEW EXPLORATION METHODS FOR PLATINUM AND RHODIUM POOR IN BASE METAL SULPHIDES
NEXTPRIM

(EC Contract BRE2-CT92-0302 - Project BE-5793)

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III. ABSTRACT

A multidisciplinary approach has been applied to four subeconomic deposits of platinum metals in order to propose a new model of formation for platinum group element (PGE) deposits devoid of significant base metal sulphides (BMS). The aim was to facilitate the identification of new targets for PGE exploration. Two of the deposits occur in Albania, in the Tropoja and Bulqiza massifs respectively; these belong to an ophiolitic belt created in an oceanic environment during the Upper Jurassic. The other two deposits occur in Madagascar, in the Andohankiranomena and Lavatrafo ultramafic massifs. respectively; these have been emplaced in a pan-African rifted zone.

A Pt-rich chromitite type of mineralization has been defined from the Andohankiranornena and Tropoja deposits where PGM are mostly included in chromite. A PL- and Pd- rich dunite type of mineralization has been defined from the Lavatrafo and Bulqiza massifs where PGE mineralization is associated with the interstitial material between olivine grains.

PGE distributions in these four deposits show contrasting patterns that are related to distinct mineral assemblages. High Pt and Rh contents (Pt up to 21 g/t), and high Pt/Pd ratios (> 5) in Tropoja reflect the presence of Rh-rich isoferroplatinum and other Rh-bearing phases. The relative enrichment in Ir, 0s and Ru of the Andohankiranomena deposit is due to the presence of sulphides, sulpharsenides and alloys carrying these elements, which coexist with Pt- arsenides and sulpharsenides [(Pt+Pd) <2 gh)]. A Pt/Pd ratio close to 1 in Lavatrafo [(Pt+Pd) up to 8 g/t)] results from the presence of sperrylite and various Pal-bearing phases (arsenides, antimonides, tellurides). A low Pt/Pd ratio (= 0.3) in Bulqiza [(Pt+Pd) up to 11 g/t)] maybe explained by the presence of pentlandite as the main PGE carrier (Pd = 0.5 wt.?lo).

It is also clear from experimental data, that there is a general tendency for Pt to be saturated in BMS and to crystallize as discrete phases resulting in Pt-alloys (Tropoja} and Pt-rich intermetallic compounds (Madagascar}.

Platinum-iron alloys are the main phases in PGE deposits poor in 13hlS. The first system investigated was Pt-Ir-Fe-S, and the related subsystem Ir-Fe-S. Because of low reaction rates, only the isothermal sections at 1000”C and 11 OO°C could be completed in the first case, 800°C was added in the second case. The Pt-Fe-Ir-S system is a good geothermometer for ore deposits of the Pt-Ir association and its overall composition is an indicator of S fugacity. The association of I?t-rich osmiridium and Ir-rich isoferroplatinurn found in an Albanian heavy concentrate is relevant to this system of which there are only few other examples (New South Wales and East Siberia).

Pt-Rh-Fe alloys coexist with immiscible sulphide melt in the system Rh-Fe-Cu-S. Low-Rh Pt_3Fe and PtFe (and Rh-poorer a Rh-Fe) coexist with a low-Rh, high Cu melt. whereas the Rh-rich Pt alloys and Rh alloys associate with Rh-rich melt (at least 20 at. % Rh in melt). Natural phases quoted in this report suggest that both types of associations are present in the Tropoja deposit. Some discrepancies may be pointed out between the natural and experimental systems. Cu- rich alloys are widespread in the natural deposit. and absent in the experimental system; crystallization products of melt associated with alloys are Rh- and Cu-rich in the natural deposit. From the study of the partial Cu-Rh-S system which serves as a sulfur-fugacity indicator in the range 900”-500”C, locally high sulfur fugacity conditions may have been developed even in the low-sulfur assemblages.

No evidence supports the existence of a geochemical halo around the PGE reef in Albania or around the PGE mineralized bodies in Madagascar, Major and trace element distributions reflect variation in the proportion and composition of mineral phases belonging either to the early mineral assemblage or to Iater interstitial material, notabl y in the Pt- and Pd- rich dunite type of mineralization.

However, in Madagascar, strong weathering of drill cores (down to 80 m in Lavatrafo) has locally modified the originaI distribution of trace elements. This is eviden[for Ce and S. Sulphides, Pd phases and, to a lesser extent, sperrylite have been locally replaced during secondary alteration. PGM are probably transformed into oxides. The predominance of HzO and COZ among the most volatile species is in accordance with the petrography of the samples, where hydrous and carbonate minerals form a significant portion of the rock. Low temperatures of alteration are also deduced from the high 81 K2 values.

In all the studied targets, hydrothermal metamorphism and recrystallization occur during the cooling of the intrusions. Reequilibration temperatures in the range 700-720”C. compatible with granulite facies conditions, are deduced from plagioclase-orthopy ~oxene pairs from a barren intrusion in Madagascar, Later, the original ma,gmatic and metamorphic assemblages have been extensively altered under green schist facies conditions. A chloride-rich mineralogy appears to have developed as a result of this hydrothermal metamorphism. This would support the absence of sulphides, possibly attacked by a secondary Ci-rich fluid, the substantial change of the metal/S ratio. and local PGE remobilization.

No major isotopic variation can be related to the emplacement of the PGE when sulphur isotopic data are considered. /n situ sulphur isotope data from Madagascar and that obtained from Albanian mineral separates (- 4.4< 8s^{4}S < + 2) are compatible with a mantle origin, as are oxygen isotope data on silicates and oxides from mineral separates and in *situ* analyses.

Influence of a crustal component is obvious in the Madagascar intrusions when radiogenic isotope data are considered. All the basic rocks are characterized by relatively high Sr [> 0.7 13] and Nd (> 0.511] isotopic ratios. However, based on mass-balance calculations, modification of the Sr and Nd isotopes was due to intensive metasomatism in the source area of the silicate melts from which both barren and mineralized intrusions were formed,

The existence of two distinct radiogenic components at the time of PGE mineralization is suggested from in situ analyses of Re-Os isotopes from an Albanian heavy concenwate. There, a more radiogenic 1870s was found in an Os-rich alloy around an Os-bearing laurite grain. This is best interpreted as mantle-derived heterogeneity in the melt from which they formed. No evidence for any large scale imput of highly radiogenic “crustal” 0s has been found.

In all the studied targets, the ore deposits have often behaved as a closed system with respect to PGE since the late magmatic stage, as illustrated by the strong chemical zoning of phases, despite much evidence for mineral recrystallization and replacement. Once formed, the ore deposit cooled progressively and subsolidus reactions occurred.

From field data, we suggest that the noble metals became concentrated in several distinct ore horizons of the basic-ultrabasic complexes. A fluid-driven multistage process is thought to be responsible for the formation of chromite, sulphide, PGM and gold mineralization. The first stage corresponds to the formation of Pt-barren chromite deposits at depth; the second stage to the deposition of Pt-rich chromitite in the upper chromite Ievek, and the third stage to the formation of Pt- and Pal-rich deposits in silicate rocks, locally associated with disseminated sulphides. Gold mineralization discovereci during this project is clearly related to this late stage.

Considering the distinct ore horizons present in a basic-ultrabasic complex. fractionation of noble metals occurred from a lower mineralizing site to the upper one. However, the mechanism whereby the noble metals become concentrated and reach the different levels is not yet well understood. Of particular importance is the presence of compounds other than S in the silicate melt, such as As, Te, Sb and Bi, which chan:e drastically the PGE contents in the base metal sulphides and the PGE distribution in the bulk rocks.

Prospecting guides are directly deduced from the proposed models. Pt- and Rh-rich horizons are to be found from the upper chromite layers up to the overlying silicate rocks, where the behaviour of the interstitial material is of critical importance. lrI al 1 the cases, the absence of significant BMS concentration does not preclude to the presence of Pt- and Pd- concentrations.

IV. INTRODUCTION

Platinum Group Element (PGE) mineralization (0s, Ir, Ru, Rh, Pt, Pd) is invariably associated with basic and ultrabasic rocks, either as more or less continuous horizons in layered intrusions (Bushveld, Stillwater), as by-products of massive sulphide deposits a[the margins of the intrusions (Duluth, Noril’sk) or as irregular diffuse bociies in “Alaska~-type” complexes (0’wendale, Australia; Tulam~en, Canada; Far East intrusions, Russia],

The origins of platinum-group metals in layered intrusions, which form economic deposits along with base metals (Fe, Ni, Cu), is based on the hypothesis that PGE’s we preconcentrated by sulphide - silicate liquid immiscibility. Consequently, all exploration methods focus on locating horizons that are enriched in base metal sulphides (BMS). These PGE deposits associated with BMS are characterized by relatively 1 ow PL/Pd ratios and by a modest enrichment in Rh.

Discoveries of PGE. mineralization in ophiolites (21 glt in Albania) and in rifted continental ultramafic intrusive (8.4 gft in Madagascar), and studies of mineralization associated with Alaskan-type intrusions, have demonstrated the existence of PGE mineralization without an associated base metal sulphide enrichment. Hence, the origin of this type of mineralization is incompatible with the stdphide - silicate immiscibility model. In addition, this type of mineralization is characterized by higher Pt/Pd ra~ios and significant Rh enrichment, compared to PGE-rich sulphide deposits. This is attractive from an economic point of view,

PGE mineralization devoid of significant BMS will not be detected using classical exploration methods. New techniques must therefore be developed and tested. The proposed research was directed at developing a model for the genesis of Pt- and Rh- rich PGE concentrations in the absence of significant sulphide mineralization, to find effective prospecting tools. The development of a new model has involved:

(1) the search for, and characterization of geochemical halos around targets discovered during previous EU and national programs. The geochemical halo would result from fluid-wail rock interaction during the ore-forming process. Its presence may be detected by a specific distribution of rare earth elements, from the composition of gaseous carbon species, the abundance of high valency incompatible elements, and from characteristic stable and radiogenic isotopes.

(2) The development of analytical techniques to determine the PGE distribution in Pt-poor host- rocks, the volatile metalloids, the relevant stable and radiogenic isotopes. and (in situ)the oxygen and rhenium - osmium isotopes .

(3) The investigation of mineral assemblages carrying the PGE mineralization and that of host rocks to obtain textural and mineralogical information suitable for the development of new extraction methods.

(4) The acquisition of experimental data on Pt- and Rh- systems poor in su]phur. to determine PGE parageneses for geothermometry and mineral equilibria. The S-poor sides of the Pt-Ir-Fe-S and Pt-Rh-Cu-Fe-S systems were investigated during the project.

V. TECHNICAL DESCRIPTION

This section outlines the different approaches and techniques which were developed during the project.

Detailed logging and sampling (about 350 and 200 samples from Madagascar and Albania, respectively) of existing drill cores was carried out for three selected intrusions (Bulqiza, Lavatrafo, Andohankiranomenaj, representative of two different tectonic environments (the oceanic environment in the A1banian ophiolites, the rifted complexes in Madagascar). Sampling was carried out in the Tropoja massif (Albania) alori: a section at Bregu i Bibes and in upper chromite deposits. The geological setting of the Pt-mineralized zone in the Tropoja massif was re-examined during sampling.

Material from the surrounding intrusion was collected in each location in ode r ro characterize ~he composition and extent of geochemicaI haloes. Sampling was carried out with respect to the location of the mineralized reef (Albania) and ore bociies (Madagascar) and according to Iithological variation. In Madagascar, samples were taken from drill cores ADKC 1 and AI?K C2 (Andohankiranomena massif) and from drill cores LVF C 1 to LVF C8 (Lavatrafo; Ohnenstetter and Ohnenstetter; field report 1993). Approximately 15 cm of split core (5-8 cm in diameter) was taken for geochemica! analysis and thin sectioning. Powders were prepared to be routinely analysed for PGE. base metal and other elements at X-Ray Assay Laboratories, Don Mills, Ontario.

Once the noble metal distribution was known, Pt-enriched and barren sainp]es itere selected for complementary analyses (PGE, REE, stable and radiogenic isotopes) as i{e 1 [as for mineral phase separates, and polished section preparation. Analyses were carried ou[using the same samples. Special precautions were taken for the Madagascar samples in order that they could be analysed for ultra-trace components (rare gases and organic compounds).

Mineralogical assemblages of the ore-forming systems were determined from the four studied intrusions using thin and polished sections. Thin sections were prepared from most of the samples, and polished sections of selected Pt-mineralized rocks and of rocks carrying disseminated chromite and sulphides. Rock texture and the crystallization order of silicate, oxide, sulphide and PGM phases, as well as the mineral phase equilibria of the successive stages were tentatively determined after observations using optical microscopy and scanning electronic microscopy (SEM). Detection of constituent elements in PGM were carried out using SEM.

After the SEM examination, mineral phases were analyzed with a Cameca SX 50 electron microprobe at Orh$ans and Manchester. For **PGM analyses, the conditions were** as follows: acceleration voltage 25 kV, beam current 20 nA, counting time 6 seconds. The standards used were: Cr_20_3 for Cr, FeAsz for As, pyrite for Fe and S. Sb_zS~ for Sb, and pure metal for the other elements. The X-ray lines used were Kcx for Ni. Cu. Fe, Co, Cr and S, La for Sb, Te, Au, Rh, Ir, Pt and Ru, and LB for 0s, Pd and As: A PAP correction program was used (Pouchou and Pochoir, 1991). For the study of gold-bearing arsenopyrite, counting time was 12 seconds for the elements, and 60 seconds for gold, Gold was also analysed by ICP-MS (Plasmaquad PQ2) using a laser probe (SPECTRON SL 402-266 rim), The detection limit for gold was< 10 ppm.

The procedure for synthesis experiments was based on the study of dry condensed sulphide systems. The samples were weighed out using analytically pure elements sealed in evacuated silica glass tubes. After annealing at 300°C for a week, charges were annealed at the desired temperatures for a period of approximately 30 days. If the desired temperature was under 800”C, charges were reground after the first anneali n:, homogenized and annealed in evacuated silica glass tubes for a second period. Then, after rapid quenching in cold water, the products were studied in polished section in reflected Iight and by means of electron microprobe analysis.

Reactivity problems were present in all assemblages at 500°C and below. In some cases, aggregates were very fine and multiphase and solid phase rang-es couid not be established with certainty. Systems at higher temperatures contained distinct solid phases, melt, etc.

A JEOL Superprobe 733 was used in wavelength-dispersive mode with an on-line correction programme. $CuFeS_2$, synthetic PtS and metallic Rh were used as standards: analytical lines were Ka for Cu, Fe and S; La for PGE. The phases were analysed by means of (1) point analyses on solid phases; (2) sweeping the beam over limited areas on solidified melts.

Results of microprobe analyses were plotted into 3- and 4-phase systems. The first estimated compositional boundaries of alloys, solid solutions and liquids were confirmed by further experiments,

The Pt-Ir volubility was determined in Pt-Fe alloys and its usefulness as a geothermometer in the Pt-Fe-Ir system determined. The volubility of Rh in Pt-Fe alloys as a function of T, fS_z and Cu activity was established experimentally.

Analyses of noble metals were obtained by instrumental neutron activation analyses (INAA) and ICP-MS. During the project, an analytical procedure to obtain PGE analyses by ICP-MS (Ru, Rh, Ir, Pd and Pal), using Te and Se preconcentration before analysis, was developed. The threshold of detection is < 1 ppb using the ICP-MS method. As analytical limitations derive from the blanks used, several tests were made to measure the PGE content of the starting solutions used, and to purify acids. Furthermore, isotopes have been selected to avoid possible interferences [I‘) I Rli. ^{1}‘)^{2}**Rli.**

103R~, [O~pd, 106pd, [~8pd, 1911r, 1931r, 194pt, 195pt, Igbpt]. Cornparable results Were obtained using ICP-MS and INAA methods. Lavatrafo samples were the first to be analysed by ICP-MS. Other PGE analyses were completed by INAA.

Trace element analyses were carried out by INAA using two separate irradiations : one with total flux (lO~s n/s/cm2) to determine Cr, La, Ce, Sm, Eu, Yb and Lu, and the other with epithermal neutrons (1014 n/s/cm2) behind a Cd filter to determine the other elements (Tb, Ir; etc.). This second irradiation method also enabled us to verify the La. Ce, Sm, Eu and Yb concentrations. This method was applied to the LVF C8 drill core (38 sampIes) and to selected Tropoja and Bulqiza samples (15 samples),

19 dunites from the Bulqiza massif were analyzed for major and trace elements b] XRF at the University of C1ermont-Ferrand.

The origins of the PGE mineralization and the extent of the interaction zone between magma and mineralizing fluids were determined from isotopic studies. The temperature and source of the fluids was determined from oxygen stable isotope (^{1}80/160) a-nalyses of bulk-rocks and silicates in PGE-enriched and barren rocks.

A chromite grain from the Bushveld UG-2 layer was used as a standard for oxygen isotope analyses of chromite, after indications that the UG2 chromite has a homogeneous signature using the Manchester ion probe and the laser fluorination method performed at BRGM. However, the matrix and standardisation problems associated with the Cr-spinels of Madagascar proved extremely difficult to resolve. and as an alternative approach, oxygen analyses were performed using traverses of LVF C8 olivine.

The laser fluorination method was used on chromite grains which are the single residual phase in strongly weathered rocks from Madagascar. At first, severa[tests were carried out to get oxygen isotope results consistent with that obtained from conventional techniques. The main modification of the conventional line to analyse [he refractory spinels was to check the fraction size of the chrornite separates. In order to obtain a total chemical attack, the sample should be crushed very finely, fine enough to floated in acetone. Contamination by the crusher is avoided by using a carburrendurn mortar. Good homogeneity was observed using this method.

Single-zircon ages were determined using the Pb evaporation method and mass spectrometry. Likewise the origin of the mafic-ultramafic complex hosting the Pt - mineralization was defined by combining stable isotopes and S m/NTd who le rock isotopes.

Secondary and backscattered electron maps were prepared to aid second ar: ionization mass spectrometry {SIMS) using the ion probe to analyse the Re-Os isotopes, 0s isotope studies were restricted to the Albanian samples because of the scarcity ancl small size of the Os-bearing minerals in Madagascar. Coarse Os-rich grains t~ere recovered from a heavy concentrate obtained during the field excursion in Albania. Bulk and in *situ* isotopic analysis of sulphur was carried out to determine the origin of the sdphur component.

The carbonic fluids [essentially C0$_2$ and CH$_4$) as well as H$_2$0 may pla~ a significant role in the transport and deposition of PGE, so these components ~;em anal ysed using gas chromatography - mass spectrometry {G C-MS) st udie.s carried OLI r using thermal decrepitation and pyrolysis (to 850*Q. ATew analytical methods (extraction by step-wise heating) was developed during the project.

Samples were analysed on a Hewlett Packard 5890 gas chromato:raph (GC] coupled to a VG TH19 quadropole mass spectrometer. 5- l(hnm sized chius of samp~e were loaded onto a sili~a W061 support ;nside a high purity silica tube. which ~(as inserted into a variable temperature SGE pyre-injector. The sample was then step-heated and decrepitated under a continuous stream of helium. The transfer line from the pyrolyser to the GC column was maintained at a constant temperature of 300°C.

Initially, the project planned to determine noble gas contents by mass spectrometry. In an attempt to reduce the extent of any air contamination, it was decided to examine the potential for in-situ analysis using a new laser-based gas extraction system being constructed and developed at Manchester. Over the last 12 months, a fibre optic **system** microscope and laser port have been added to the accompanying VG5400. The sulphides included in chromites will be step-heated in vacuum with the IR laser to release any trapped fluids associated with the sulphide-forming event.

W. RESULTS

Field characteristics of the PGE-enriched zones

West Andriamena intrusions, Madagascar

PGE-rich zones in the Andriamena areas were identified in small intrusions (< 2 km x 1 km) linked to magma injections in mobile zones of Archean age at different depths [EC Contract MA IM-0008-F(CD) 1992] (Fig. 1).

The basement at West Andriamena was affected by two tectono-metamorphic events. The first was generated during regional metamorphism of granulite to amphibolite facies. Isoclinal folding is associated with S 1 foliation transposed onto the primary SO layering.

The second event is marked by the development of subvertical N-S shear zones both in basement and the intrusions. Amphibolitic to greenshist facies metamorphism is associated with shear zones. This second event is thought to be responsible for the emplacement of the ultramafic complexes under low grade granulite facies (< 5 kb). Evidence for a N-s strike-slip system come from the Sigmoidal patterns of the intrusions. the asymmetrical distribution of lithological facies and the presence of fractures of variable orientation ranging from distensive to shear and filled by magma.

The ultramafic intrusions contribute significantly to the growth of the continental crust during a Pan-African rifting. At the surface, sections of ultramafic bodies represents about 409i0 of the shield formations, and dioritic to granitic intrusions, about 1570. The West Andriamena intrusions were emplaced at a higher structural level than the North Andriamena intrusions hosting large Pt-barren chromite deposits which are severely folded. Remobilisation and rejuvenation of the continental crust occurred during injections of mantle-derived magmas at different dephts. This led locally to partial melting of continental crust followed by extraction of dioritic to granitic magmas injected in upper parts of the continental crust. The ages obtained on dark zircon vary between 2.4 and 3.3 Ga confirming the age of the basement (Fig. 2). Pale euhedral zircons with no zoning from the reputedly Archean basement, gave, over several steps, ages of around 770-790 Ma. The post -intrusion late granite shows a high content of inherited basement zircons (ages of between 2.2 and 3.2 Ga) and zircons related to the granite emplacement with a younger age (762 * 17 Ma). Zircons from mineralized and barren intrusions gave ages between 777 + 12 Ma and 786 t 23 Ma.

Two types of complex have been defined in the West Andriamena area according to their shape, constitution and Pt-mineralization (Fig. 1). The orthopyroxenite-type complex or Andohankiranomena-type intrusion has a dome-like shape. It is composed of

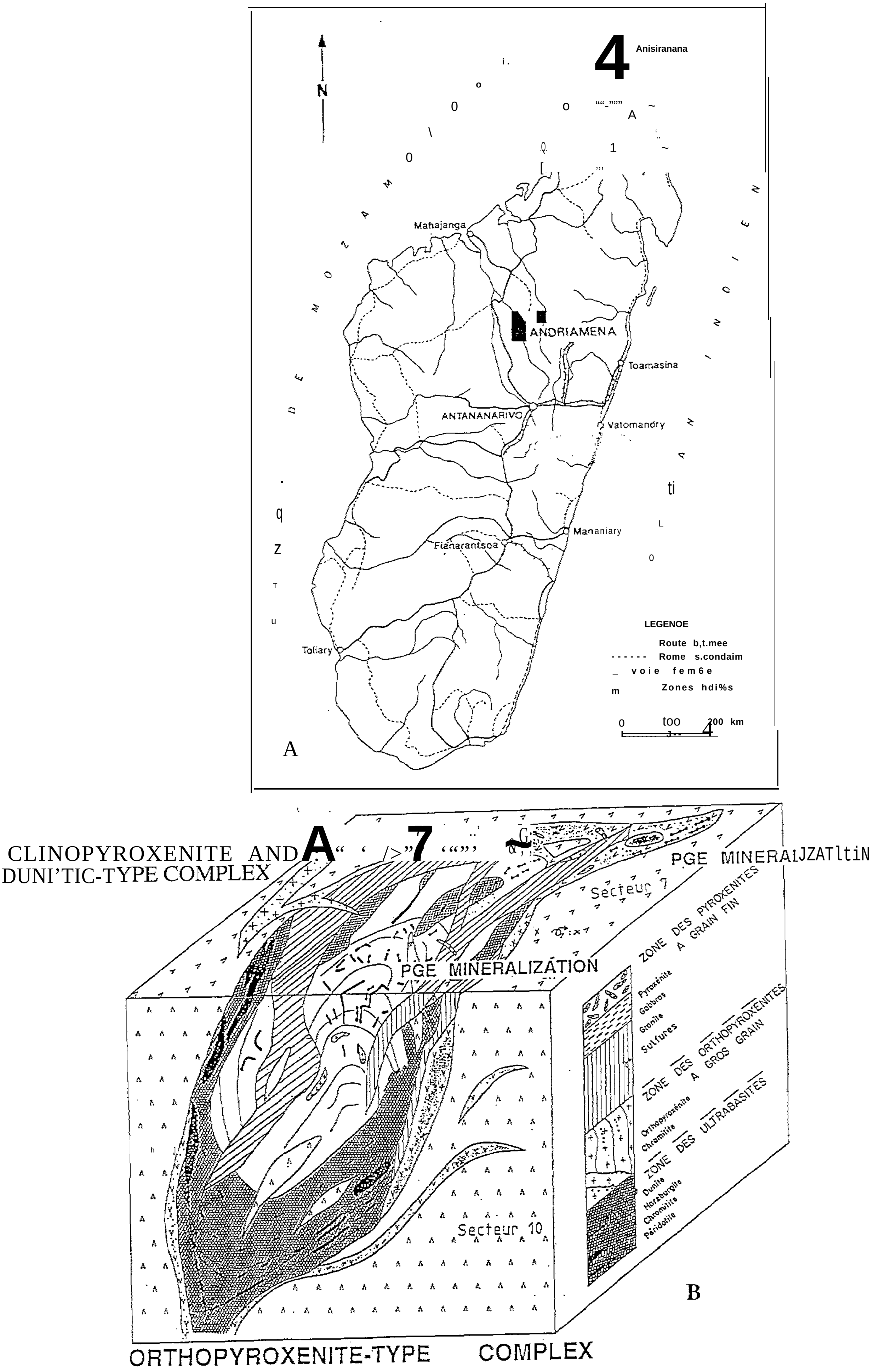


Fig. 1 A, Sketch map showing the location of the studied area West of AndrimIena in Madagascar. B, Reconstitution of the West Andriamena complex=.

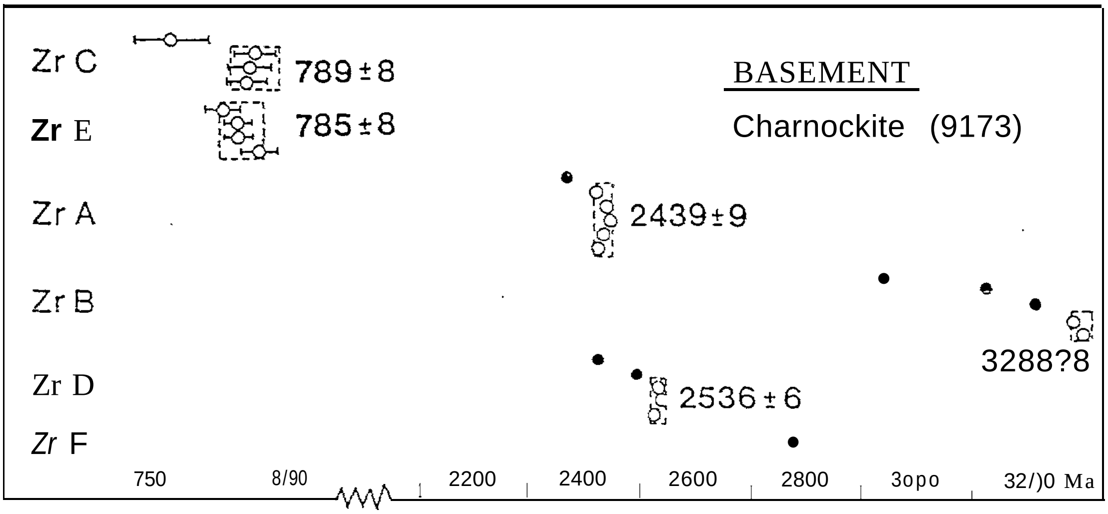


Fig. 2 A, Distribution of ages obtained on zircons of sample 9173 from the gramuiitic basement country rocks of the ultrabasic intrusions.

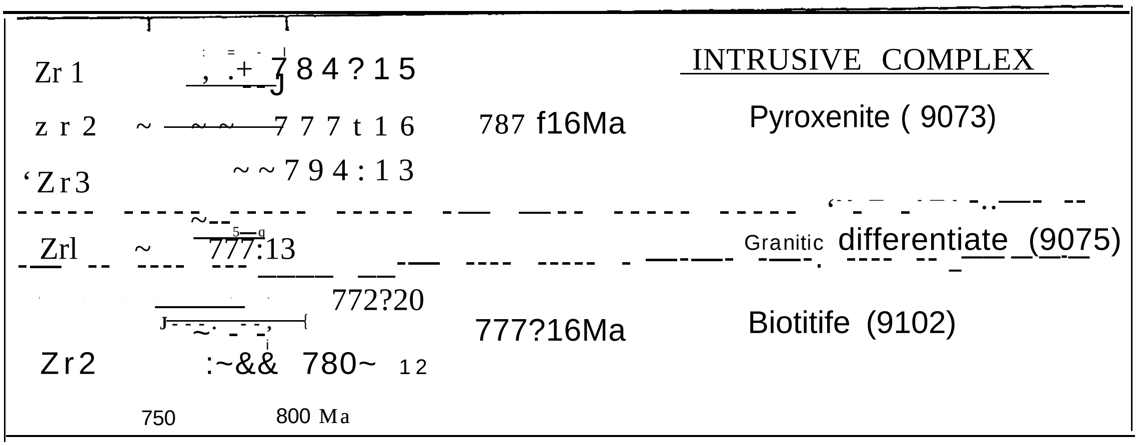


Fig. 2 B, Distribution of ages obtained on zircons from the three analyzed samples of [he Bemongikely ultrabasic intrusion.

(1) a zone of coarse grained peridotite cut by massive chromite dykes; (2) a **zone of** orthopyroxenite and related chromitite veins having a dyke setting; (3) a marginal zone of fineci-grained pyroxenite. Pt-mineralization occurs in the orthopyroxenite zone and is related to the presence of chromite seams. The dunite-type intrusions or Lavatrafo-type intrusions have a funnel-like shape filled mostly with dunitic rocks and minor orthopyroxenite and pyroxenite. Chromite seam are exceptional whereas interstitial sulphides are locally well developed as in West Lavatrafo. Narrow amphibolitized gabbroic rocks occur in dykes cutting dunite and pyroxenite.

The West Andriamena intrusions are usually strongly metamorphosed. Preserved fine-grained pyroxenites are recognized usually at the margin of the intrusion. Relict dunite has been recovered only in drill cores LVF C8. Tremolitite is a common facies after dunite, harzburgite and orthopyroxene, The presence of orthopyroxene was deduced from the presence of relict shapes in Andohankiranomena. Fresh orthopyroxene was observed in interstices at Lavatrafo in dunitic rocks.

Evidence for granulite facies metamorphism is present in pyroxenitic rocks. Retromorphism in the amphibolitic facies is widespread in the intrusive, more particularly in dunite and orthopyroxene-rich rocks occurring in the core of the intrusions. Reaction zone with amphibolite and biotitite bordering the granitic plugs are related to metasomatic reactions during the emplacement of granite, Low temperature hydrothermal processes are visible along late shear zones and are responsible for veins filled with serpentinite, calcite, magnesite, chlorite, which cut dunite still having fresh olivine. Rocks are usually deeply weathered even at depth along drill cores.

Pt-mineralized rocks have been studied from selected drill cores of the Andohankiranomena and Lavatrafo intrusions.

Pt-rich chromitites of Andohankiranomena

Hydrofracturing is responsible for the setting of most of the chromitite seams and dykes of variable size and orientation in the orthopyroxenite zone. The usual chromite dyke orientation is NW-SE to NNE-SSW, subparallel to the elongated intrusion. Chromitite are massive to submissive. Oblique dyke on this direction and transverse dyke (N 10O°C J also occur. They are filled by disseminated to orbicular and massive chromitite. Flat dykes of disseminated to massive chromite are thin and more often sheared.

Drill core ADK C 1 in the Andohankiranomena intrusion- has been divided into three zones according to the proportion of the different lithological facies. Although all the primary magmatic phases, except the chrome spinels, are completely replaced by amphibole (cummingtonite and tremolite), the primary rock texture is still recognizable in hand specimens. The upper two zones have anomalous Pt and Pd contents.

Detailed observations indicate that the host chromite dyke may be dunite. Harzburgite and coarse-grained orthopyroxenite. Chromite-richest zones correspond to the higher Pt and Pd anomalies. Anomalous Pt and Pd contents also occur in silicate rocks having only disseminated chromite. This is in agreement with the general high background observed in orthopyroxenite zone of the Andohankiranomena intrusions. When the texture is preserved in weathered rocks, chromite occurs in interstitial areas between orthopyroxene.

Pt-mineralization of Lavatrafo

Mineralized bodies may be defined in two Lavatrafo-type intrusions from the distribution of Pt+Pd anomalies along trenches and drill cores. One drill core was more particularly studied because of the presence of quite fresh rocks from a depth of 20 m. Detailed studies indicate the existence of two major magmatic pulses, resulting in dunitic rocks in both cases, The boundary between the two magmatic pulses is marked by a lithological change with aclearincrease inorthopyroxene from pyroxene- and BMS-bearing dunites to pyroxene-rich BMS-bearing dunites.

A zonation is defined in the dunitic intrusive according to the extent of depth, the presence of disseminated sulphides and spinel, and the grain size variation. The first magmatic pulse comprises three zones (zone 1 to 3) down to 77 m, and the second is in the lower part of the drill core (zone 4). Cr-rich rocks occurs in zones **2** and 4 but always in low proportion.

Both dunitic intrusive are PGE mineralized. They locally carry disseminated base-metal sulphides. Careful petrographic examination indicates that the PGE mineralization cannot be correlated with the presence of fault zones, low-temperature hydrothermal systems or the presence of spinel and base-metal sulphides.

In Lavatrafo, pyroxene (ortho- and/or clinopyroxene), phlogopite, base metal sulphides (BMS) and Cr-spinel usually occur in an interstitial position. This interstitial material contrasts with the cumulus material composed of olivine in Lavatrafo. 01 i vine shows a more evolved character towards the base of the drill core, that is towards the core of the intrusive compIex. Fo in olivine varies from Fog? down to F083.

The Tropoja and 13uIqiza ophiolitic massifs, Albania

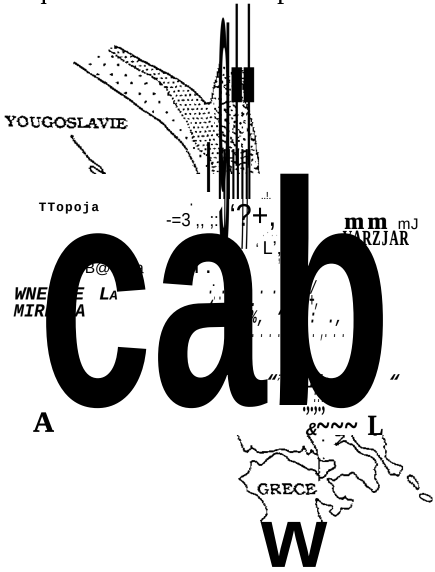
In Albania, the ophiolite belt -named the Mirdita Ophiolitic Belt (MOB)- is part of the Mesozoic Tethyan ophiolite belt, extending from Spain to the Himalayas (Aubouin and Ndojaj, 1964) (Fig. 3), The Albanian ophiolites are Late Jurassic in age (Kodra et al., 1993) as those from Western Mediterranean belt (Corsica to Austria and Ex-Yougoslavia), whereas farther east, from Cyprus to the Himalayas, the larger ophiolite masses are Cretaceus.

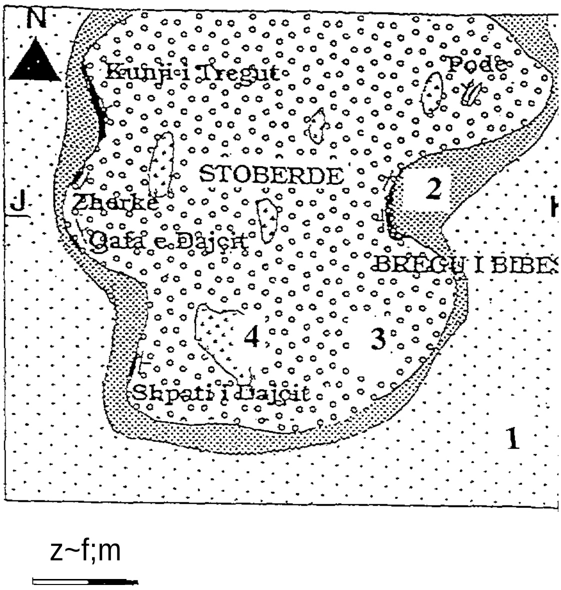
The Western-Type ophiolites, defined in Corsica, the Alps and the Apennines. show strong similarities with present-day mid-oceanic ridge rocks, whereas the Eastern-Type ophiolites, well represented by the Cyprus, Turkish and Oman ophiolites, closely resemble immature island-arc igneous rocks. Because of their geochemical characteristics. Western-Type ophiolites are thought to derive from an oceanic basin bordered by passive margins. The original setting of Eastern-Type ophiolites is much less clear. Based on geochemica~ evidence, the Eastern-Type may have been formed in an active-margin environment, being a remnant of a fore-arc or back-arc marginal basin.

In the Albanides, both types of ophiolites are found in approximately AT-S trending belts (Fig. 3) (Tashko, 1976; Shallo, 199 l). They coalesce in the northern ophiolitic massifs. The western belt showing similarities with Western-Type ophiolites, is composed of a lherzolitic mantle, plagioclase-rich basal cumulates (troctolite, gabbro) and TiOz-rich basaltic lavas (1.5-2% TiOz). Conversely, the eastern belt has characteristics close to the Eastern Ophiolites, and shows the succession of harzburgitic mantle. pyroxene-rich basal cumulates (wehrlite, pyroxenite, clinopyroxenite, orthopyroxenite) and $Ti0_2$-poor lavas with a range of $Ti0_2$ down to 0.4% in Iavas of boninitic affinities (Beccaluva et al,, 1994). These features indicate that the western ophiolitic belt originated from a magmatic source that was less depleted than that of the eastern ophiolitic belt as for the paired ophiolitic belts of Greece and Ex-Yugoslavia (Bebien et al., 1980).

Based on geotectonic reconstitution, the size of the oceanic basin rarely exceeded 5000 km, even considering a fairly rapid spreading rate of 8 cm/year. As in ~many other ophioiites, roughly AT-S trending strike-slip movements were effective during the closure of the Mirdita basin. Subvertical contacts, especially east of the Mirdita nappe, result from such tectonics. The possible role of strike-slip faults during the rifting and later. during the opening and accretion processes, is suspected as well

Fig. 3 A, Geologic sketch map showing the location of the studied area of Tropoja ar J3ulqiza in the doubIe ophiolitic belt of the Mirdita zone {Albania).





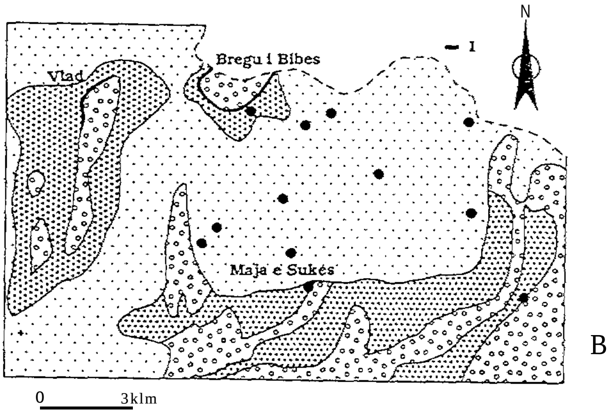


Fig. 3 B, Geologic map of the Tropoja ophiolitic massif, detaiIed map of the Bregu i Bib PGE-bearing intrusion, Fig. 3 C. 1, Harzburgitic mantle; 2. Dunitic zone: 3. Pyroxenit zone; 4. Gabbroic zone.

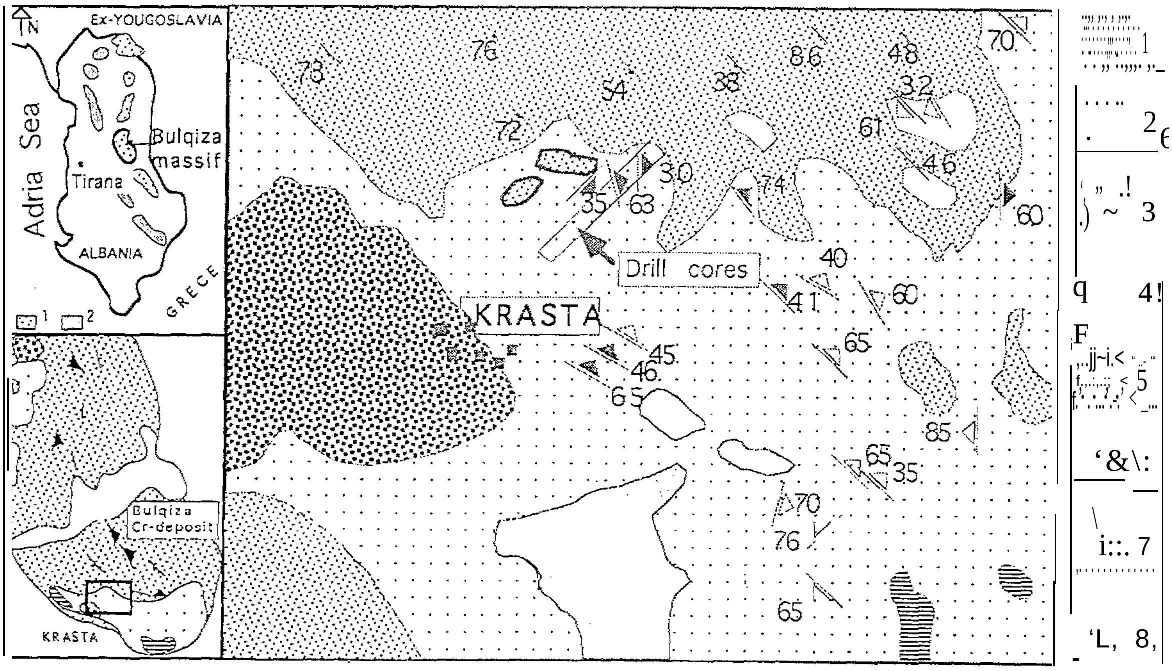


Fig 4A, Sketch maf of the location of the Buiquiza massif within the doubie Mirdita ophioliti belt (Albania]. B, Geologic sketch map of the 13uIquiza massif and location of [he Krasra area C, DetaiIed geoIogic map of the Krasta area. 1 Harzburgitic mantle sequence; 2. Up pert lMoh dunite zone; 3. and 4 Iherzolite and pyroxenite from the layered ultramafic sequence: 5

The metallogenic potentialities appear quite different for the western ophiolite belt and the eastern ophiolite belt (Cina et al., 1986), as for Western- and Eastern-Type ophiolites, respectively. No economic deposits occur in the former, whiIe the latter contain podiform chromite deposits in the deep part of the ophiolites, i.e. in the mantle and at the base of the cumulative sequence, and sulphide deposits in the upper lava sequence, have long been mined. Hence, the Mirdita ophiolites are a good example of an ophiolitic segment where the influence of the magma type on the presence and extent of deposits can be determined.

Most of the chromite is produced from the Tropoja and Bulqiza ophiolitic lmassit's belonging to the eastern ophiolitic belt, The chromite deposits are podiform in the mantle. usually towards its upper part in the so-called transition zone, or stratiform, occurring at the base of the cumulate sequence. Variations in the composition of the chromite with depth have been. pointed out in mantle deposits of the Tropoj a and Bulqiza massifs (Karaj, 1992).

The presence of platinum-group element (PGE) mineralization has long being known in Albania, where PGM were described in chromitite and from alluvial heavy-mineral concentrates (Cina, 1989), Subeconomic PGE mineralization occLux in chromitite and dunite related to crustal sequences (Ohnenstetter et aI., 199 1). A Pt-rich mineralization occurs in chromitite dykes of the Tropoja massif, due to the presence of isoferroplatinum as the main PGE carrier. A Pd-mineralization associated with base metal sulphides (BMS), mostly pentlandite, is also known in dunite between the harzburgitic mantle and the plagioclase-bearing ultramafic cumulates of the Bulqiza massif. These Pt-Pd mineralizations have been studied during the EU project.

Pr-rick chmnifites of Tropoja, Albania

The Tropoja ophioIite massif occurs in the northern area of the eastern ophiolite belt close to the Ex-Yugoslavian border (Fig. 3). A thickness of up to 10 km is deduced from geophysical data. The proportion of crustal rocks is less than 20 % of the ophio~itic massif. The Tropoja ophiolite massif shows a complete ophiolite sequence. with preserved primary tectonic features related to accretion (Neziraj, 1992; Nezira,j et al.. i992).

The mantle structure is complicated by Iate-stage folds formed during accretion processes and later tectonic emplacement of the ophiolite onto the continental crust. h mantle rocks, chromite deposits form a discontinuous subparallel belt, NW-SE trending. related to local magmatic injection zones. Rocks of the crustal sequence are better developed in the southern part of the Tropoja massif where layered cumulates with dunite, lherzolite, pyroxenite and gabbroic rocks are covered by lava units. Compared to this well layered sequence, the intrusion hosting the Pt-mineralization is characterized by coarse-grained rocks and pegmatitic dykes, especially in the vicinity of the rnineralizeci zone. Four lithologic units are defined in the Bregu i Bibes intrusion above the harzburgitic mantle:

1) A coarse grained dunitic unit with disseminated, subeuhedral spinels, up to 2 mm. usualIy located between the olivine grains. Spinel-rich veins are rooted in concentrations of spinels interstitial to olivine.

2) A pegmatitic orthopyroxenite to pyroxenite dyke unit. Dykes cut the underlying dunite or the mantle harzburgite. The density of dykes decreases in dunite and mantle farther away from the intrusion. Orthopyroxenite are locally cut by chromite-rich veins. Chromite concentration towards the core of the pyroxenitic dykes may ha~re a diffuse contact with the pyroxene-rich rocks. In this case, chrome spinel occurs in interstices between pyroxene and may form a poikilitic texture. Fast growth of spinel is **suggesteci** from engulfed and elongated grains. Rare clinopyroxene and plagioclase are also found **in** interstices between chromite and orthopyroxene.

3) A websterite unit occurs in the core of the intrusion. The dyke setting and the grain size (4 cm down to 0,5 cm) of the rocks decrease progressively up the sequence where

massive websterite occurs, Likewise, the proportion of orthopyroxene decreases upwards at the expense of euhedral clinopyroxene and anhedral interstitial plagioclase.
4) A massive gabbro unit variously enriched in iron oxides.

The direction of the foliation varies in harburgite and dunite from NW-SE to E-W. Foliation is subvertical in dunite and less inclined in mantle rocks. Dykes may be subparallel to the E-W foliation recorded in dunite close to the pyroxenite unit. or perpendicular, Lithological contacts between the main zones are subparallel to dykes. being E-W or N-S. Sheared flat pyroxenitic and chromitite sills tchanged into subvertical dykes.

The Bregu i Bibes intrusive rocks were derived from a rather small magma chamber (max. 2km long) fed by multiple dykes, the density of which decreases in the mantle farther away from the intrusion. The mineralized sequence could have been derived from an iron-rich melt as revealed by the presence of spinel and olivine ($\mathrm{F0}_{87}$) in dunite and pyroxenite richer in iron that olivine at the base of the barren cumulative sequences (Fo_{YO}. 88), and by the presence of magnetite-bearing gabbro norite. Other relevant features include the earl y crystallization of orthopyroxene before [hat of chromiferous spine 1 hosting the Pt-alloys; major crystaHization of clinopyroxene occurs later, before plagioclase.

Because of the setting of the Pt-rich chromitites in dykes, the mineralized zone shows important lateral discontinuities. R is present all around the intrusion, but is more developed close to the western and eastern side of the former magma chamber. Similar Pt-mineralization occurs in other intrusions of the south eastern Tropoja massif. Sampiing was undertaken in the pyroxenitic and chromite-rich dykes.

Pt-tnineralizafion in sulphide-bearing dunite Of Bi..dqiza

In Bulqiza, a huge mass of dunite which hosts the Pt-mineralization, separates the harzburgitic mantle from the crustal pyroxenitic or gabbroic sequences (Fig. 4). Diapiric structures are preserved in the Bulqiza mantle harzburgite, east of the Bulqiza chromire deposit, one of the biggest chromite deposit of the world (Dobi, 1981: Shalio et al.. 1989). Direction of foliation is NW-SE as the ophiolitic belt, except along transverse shear zones. Reconstitution of the ophiolite assemblage is locally complicated by intrusi~-e relationships of rocks forming the crustal sequence.

A gabbroic sequence and an ultramafic sequence may be defined above mantle harzburgite and supra-Moho dunite (Karaj, 1992). The gabbroic sequence is composed from base to top by few plagiferous dunite, troctolite, Ieucogabbro up to anorthosite. and gabbro, which may rest on mantle harzburgite, supra-Moho dunite or on the ultramafic sequence. The gabbroic sequence is usually better layered than the ultramafic sequence formed by dunite, cpx-bearing dunite, wehrlite, lherzolite, pyroxenite, clinopyroxenite and gabbronorite. The ultramafic sequence is intrusive into mantle rocks. supra-Moho dunite or in the gabbroic sequence. Dykes of pegmatitic pyroxenites belonging [o [he ultramafic sequence, cut harzburgites, chromite deposits or gabbros. Parental magimm of the ultramafic and gabbroic sequences are distinct according to REE pat Fe rns: flaf anti slightly depleted in LREE for the gabbroic sequence, more depieted in total REE. bLIt t~ it h HO LREE. depletion, for the late ultramafic sequence.

The dunitic zone at Krasta, south of the Bulqiza massif is subdivided into t~{o subzones (Lleshi, 1988): the lower subzone hosts discontinuous layered chromire deposits with massive to disseminated chromite. The size and extent of the chrorni[e layers decrease from the base to the top of the lower subzone. In the upper subzone. chromite seams are decreasing and locally bear interstitial Ni-rich sulphides (S hallo m-tci Cina, 1970). The reef is discontinuous and located at various depth below the ct-ustal sequence. The thickness of BMS- and spinel- bearing dunites may reach 40 m. Pt anti Pc!

anomalies are locally associated with BMS (Qina, 1988), The direction of the chromite layers and seams are variable [Nl 10”C; N140*C, N-S].

Serpentinization is more pronounced around the chromite seams and close to sulphide-bearing dunite (so-called black dunites). Rocks from the dunite zone were sampled in a trench and along drill cores, east of the Krasta village. Samples are composed of dunite, spinel-bearing dunite, disseminated to massive chromitite. BMS-bearing dunites (up to 3 % BMS) and BMS- and spinel- bearing dunites.

Distribution of major and trace elements with stratigraphy

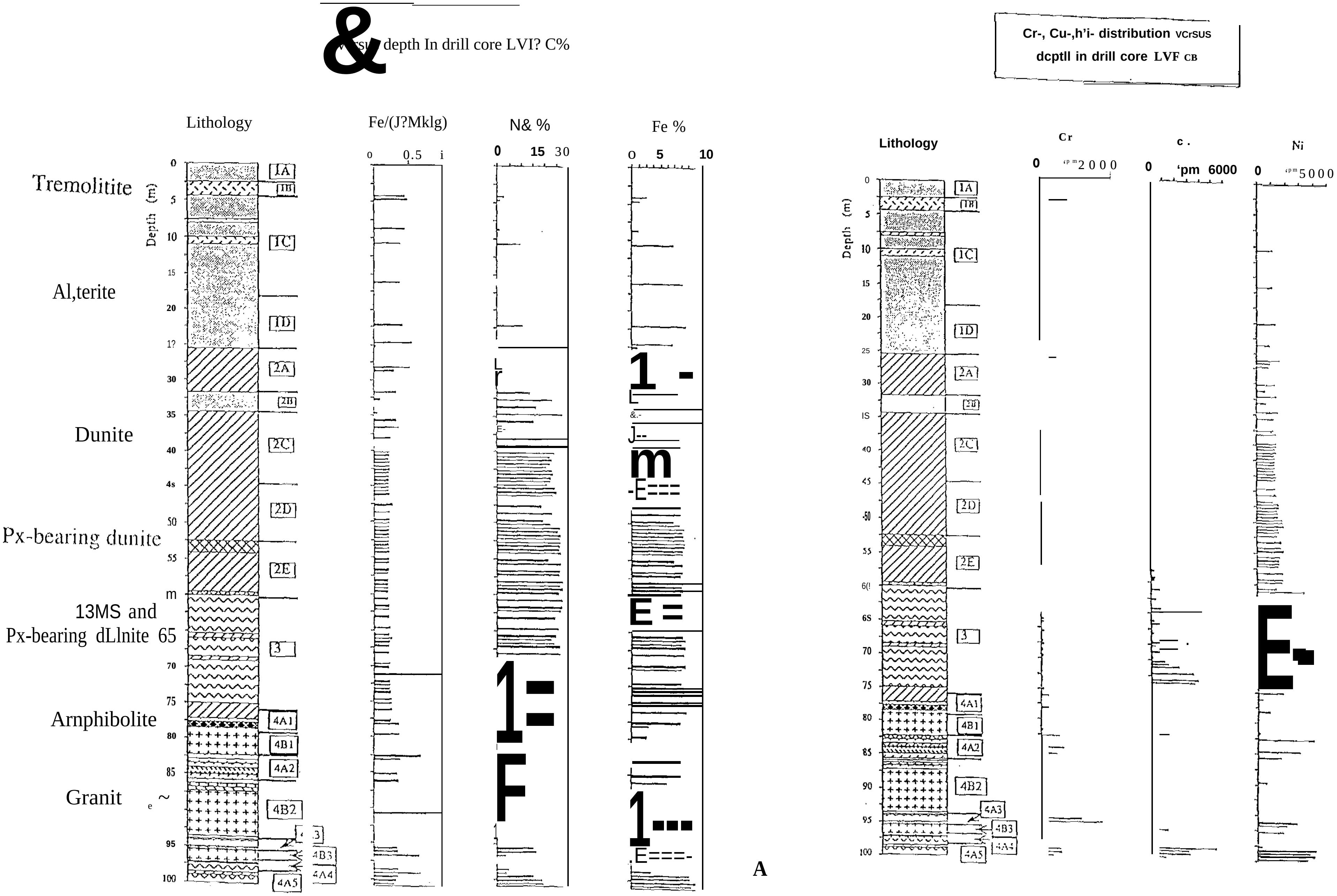
The West Andriamena target

Major and trace elements were routinely analysed in samples from the Andohankiranomena and Lavatrafo drill cores in order to detect the presence of a geochemical halo around the Pt + Pd anomalies. However, no simple element distribution around the mineralized body can be delineated.

The geochemical distribution of some major elements and base-memls is controlled by the lithological variation (Fig. 5 A and B). In drill core LVF C8, the BMS-bearing dunites are enriched in Cu and Ni, the latter element being distributed between olivine and pentlandite. Likewise, Co increases in BMS-bearing rocks, and Cr and V in spinel-bearing rocks in relation to the presence of Co-enriched sulphides and chrome spinel, respectively. Furthermore, the rocks are gradually more evolved towards the base of drill core LVF C8, with decreasing Mg/(Mg+Fe) and increasing Al, K, Na, Ti and V. This corresponds to the decrease of the forsterite component in olivine. All of these facts indicate the existence of fractionation processes inside a dyke-like intrusion, with more evolved rocks at depth and towards the western border of the intrusive, accompanied by an increase of the intercumulus material.

The Albanian target

There is a gradual slight increase in the Fe/Mg ratio of dunitic rocks and olivine from the base to the top of the dunite zone in the Bulqiza massif. This is compatible with recrystallization of olivine in the presence of a more evolved melt in the upper levels of the zone, However, such an Fe/Mg increase is not recorded for spinel-rich dunites of the upper subzone because of the strong Al and Mg enrichment of interstitial spinels. In contrast, sulphide-bearing dunites usually have a higher mafic index, coupled with high S (0.05 to 0.14 wt. %), Ni (2350 to 3360 ppm) and Cu (175 to 518 pprn) contents. CtiO content increases towards the upper dunite zone because of the presence of interstitial clinopyroxene and amphibole. Incompatible elements such as Zr ($1.9 < Zr < 3.7$) and P ($0.02 < P < 0.06$ wt. 9io] also increase with stratigraphy. The behaviour of the most fusible and incompatible elements indicates that some interstitial melt was trapped between the olivine grains, in the upper subzone to give the observed interstitial material. The trace element distribution and the chemical evolution of spinel with stratigraphy are compatible with a process of convective fractionation rather than with a diffusive process (Tait et al,, 1984).


& versus depth In drill core LVI? C%

Cr-, Cu-,h'i- distribution versus dcptll in drill core LVF CB

Fig 5, Fe and Mg (A) and Cr, Cu and Ni **(B)** distribution versus depth in drill core LVF C8 (M Igascar).

Distribution of PGE in the mineralized sampIes

Neutron Activation and ICP-MS methods were refined during the project. They were employed to determine the PGE distribution in the Pt-mineralized samples.

Madagascar targel

In the Andohankiranomena complex, Ru, 0s and Ir concentrations are relari vel y constant whereas those of Rh, Pt and Pd vary from a negative to a positive slope on the PGE patterns (1.9 e Pt/Ir < 10.3; 0,8 <PtJPd < 5,1).

In Lavatrafo, the PGE patterns is strongly positive due to lower Ru,, 0s and Ir concentrations and especially to high Pt and Pd contents. Rh is significantly hgher than Ir and Ru (Fig. 6A).

In contrast to PGE mineralization in ophiolitic chromitite, chromite-bearing samples in Lavatrafo show no preferential enrichment in Ir and Ru. Likewise. there is no correlation between PGE content and transition metal concentrations (Cr. N i. etc... 1. Furthermore, Ru is generally depleted considering Ir and Rh chondrite normalized concentrations. This could be called a “negative Ru anomaly” (Fig. 613). In the LVF Cil core, the highest Rh grade is more often found in spinel-rich dunite, more particularly where chrornite schlieren occur.

On the other hand, Pt content increases with As concentration according to a trend parallel to PtAs2. The correlation is good for As concentration above 1.5 ppm. This suggests that more than 50 To of the Pt is as sperrylite.

Albania target

The distribution of PGE in Pt-mineralized rocks from the crustal sequences of Bulqiza and Tropoja are compared with those occurring in mantle rocks.

The Bregu i Bibes mineralization is characterized by a high Pt content for a low Pci content as illustrated by the high WPd ratio (>5) and Au content. (Fig. 7)

Routine analyses of Pt and Pd in chromitite from several deposits belonging ei t her to the mantle or to the crustal sequence in the Tropoj a massif, reveal the presence of several PGE anomalies, Most of them are characterized by a high Pt/Pd ratio comparable to that of the Bregu i Bibes mineralization. The highest values are recorded in the PGE mineralized zone of the Bregu i Bib% intrusion (> 15 ppm). The range of (Pt + Pd) values in chromitites indicates a strong variation of the PGE content at a small scale in the mineralized zone.

Noble metal concentration was found in sulphide-bearing dunites from the ciunite zone of the Bulqiza massif. The (Pt + Pd) contents are subeconomic (8.7 ghl ~vi [h a Pt/Pd ratio less than 1 (0.3 < Pt/Pd < 0.6). Correlation between S and noble metals is not good. This is due locally to the transformation of base metal sulphides into al Ioys. or to the existence of PGM not directly hosted or associated with sulphides. PGM are difficult to find in these rocks because of their small size (< 3 ,um).

All the Pt and Pd deposits have an evolved character based on the (Pt+Pd+Rll) / (Os+Ir+Ru) ratio, usually higher than 1 (Fig. 8). This is compatible with noticeable PGE fractionation before the formation of the deposits which occurred in the lower ultmmafic zone hosting most of the chromite deposits.

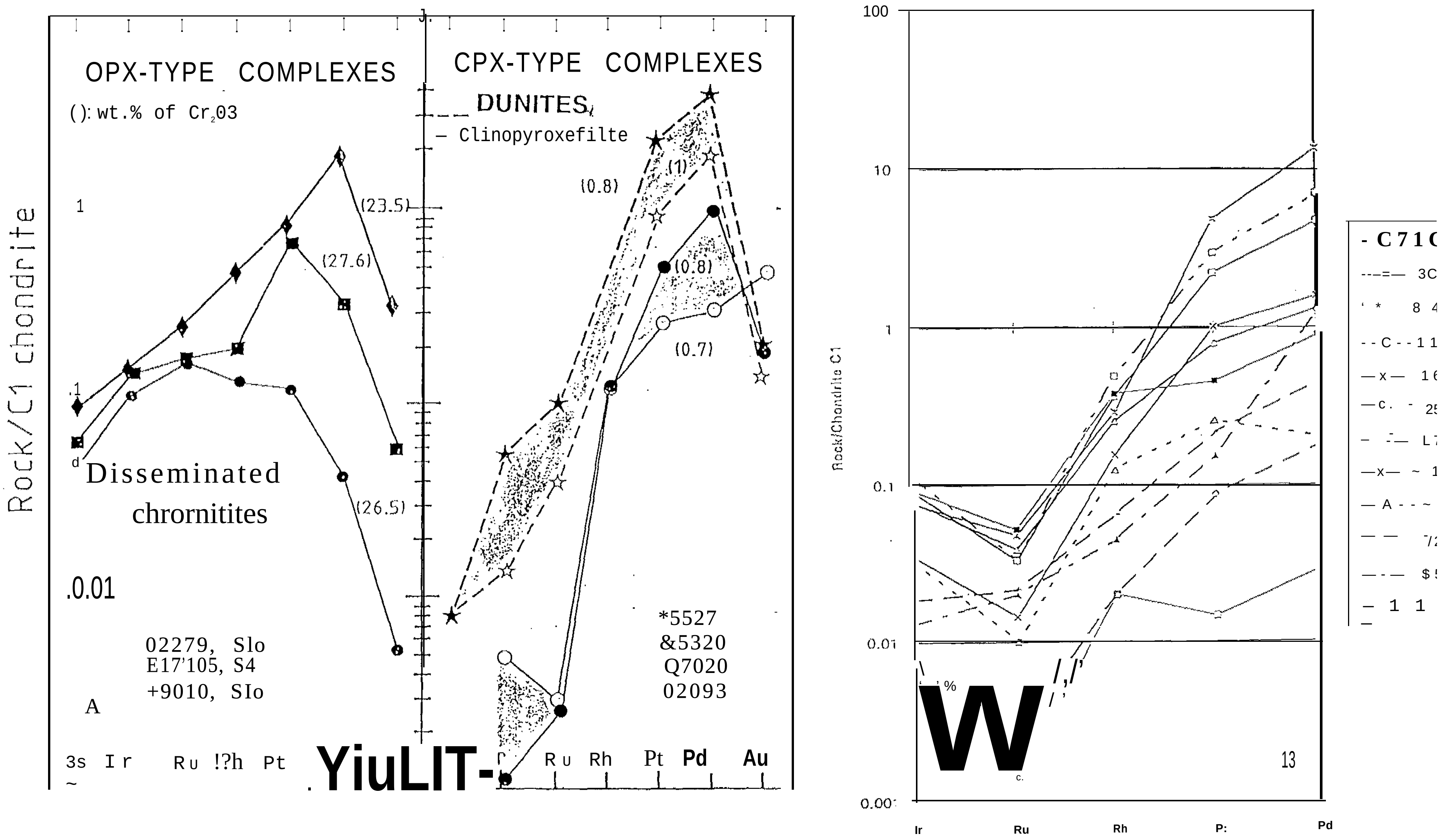


Fig. 6 A, Chondrite normalized-PGE patterns for the Opx-and Cpx-type complexes from West Andriamena (Madagascar). B, Chondrite normalized PGE patterns for dunite ZLnci weathered dunite of LVF C8 drill core from Lavatrafo (Madagascar).

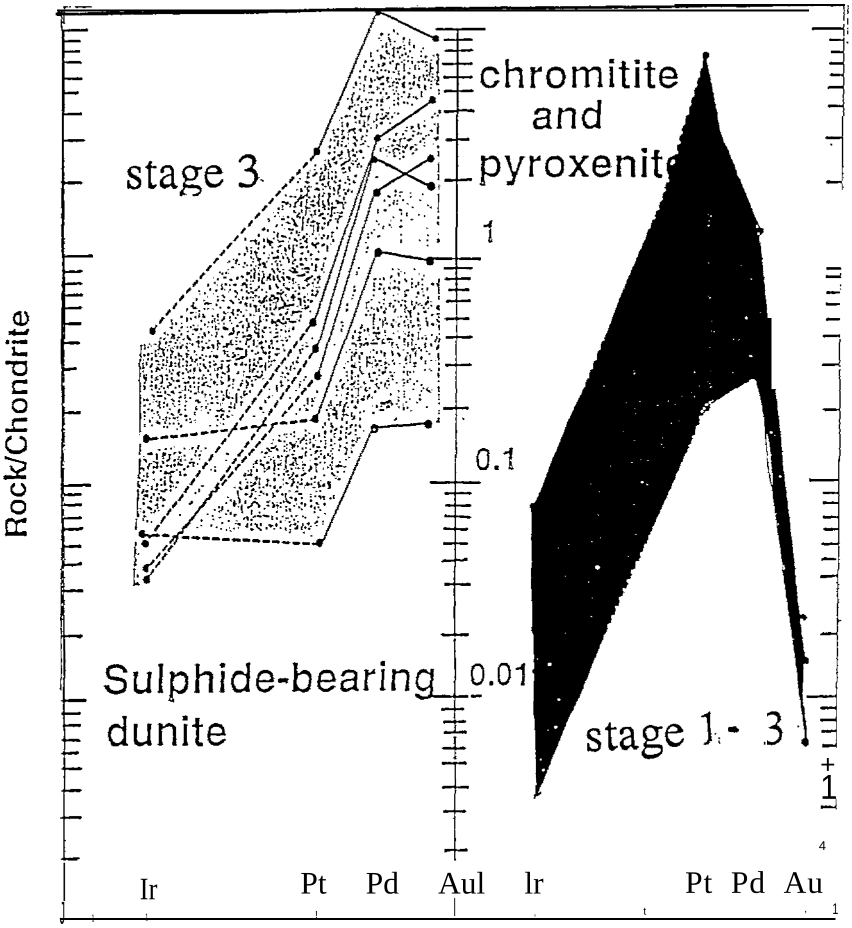


Fig. 7Chondrite-normalized PGEpatterns fo; sulphide-bearing dunitefroln B~llqLliz~aIld for chromitite and pyroxenite from Tropoj a, Albaman ophiolitic complex.

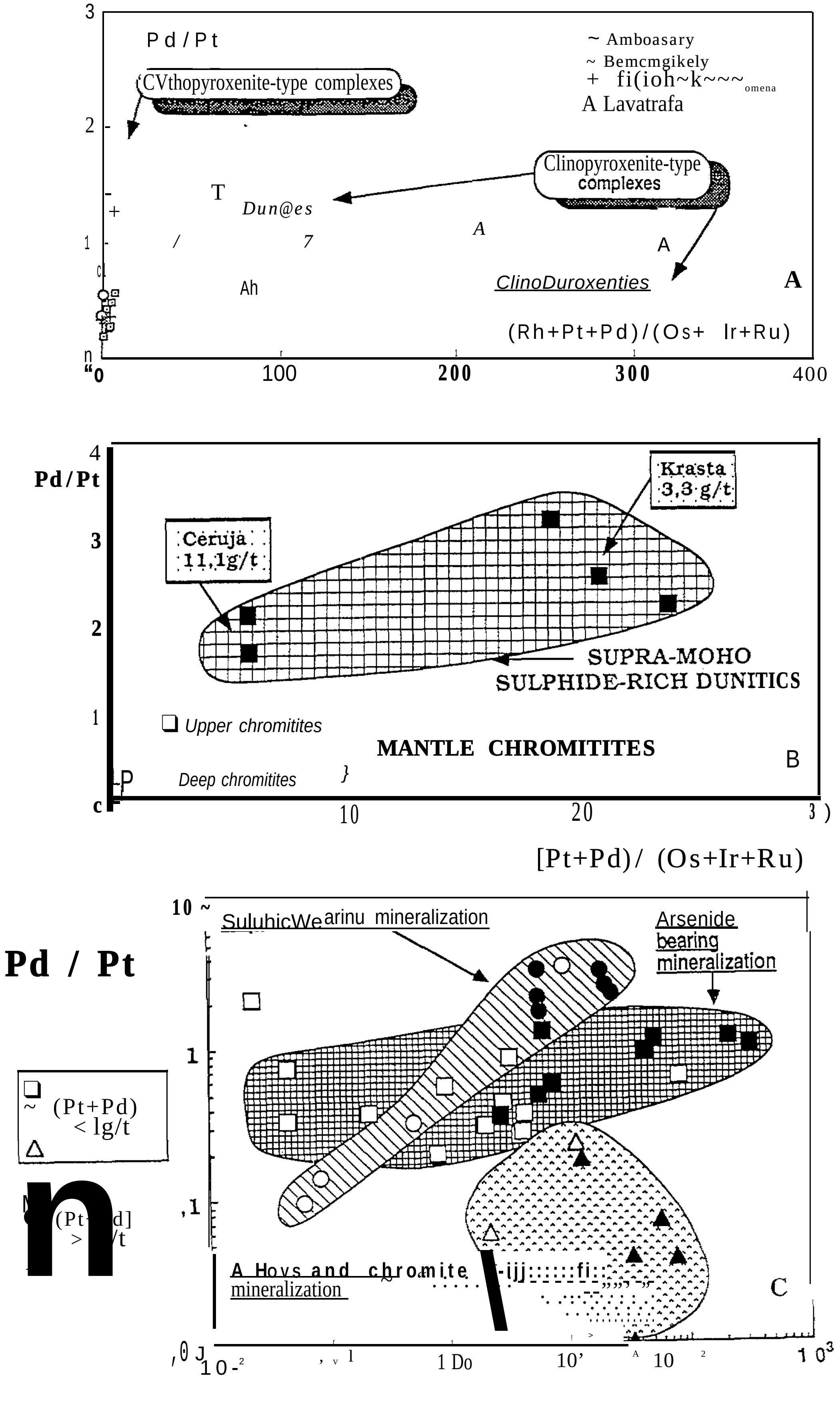


Fig. !3 A, Pd/Pt versus (Rh+Pt+Pd)/(Os+Ir+Ru) for the As-rich mineralization of Wes[Andriamena, Madagascar; **B,** Pd/Pt versus (Pt+Pdl'(Os+Ir+Ru) for the sulphur-rich mineralization of Bulquiza; C, Pd/Pt versus (Pt+Pd)/(Os+Ir+ R~l) for the arsenicle-type. sulp'nide-type and alloys-type of PGE mineralization.

PGE and gold mineralization

Gold anomalies were discovered in the Bulqiza {up to 2.1 glt). Lavatrafo (up to 1,2 g/t) and Andohankiranomena (up to 0,4 g/t) deposits (Fig. 9 A and B). The highest grade occurs in rocks carrying BMS or close to BMS-bearing rocks either in Lavatrafo (LVF C8 drill core) or Bulqiza, It is striking that the Pt-mineralized chromitite at Tropoj a, having no sulphide visible with the naked eye, has low gold content (< 10ppb).

There is a decoupling between the Rh, Pt and Pd anomalies and that of gold revealed by routine analyses from rocks sampled each 0.5 m along the Lavatrafo drill core. More especially, Rh and Au anomalies show contrasting behaviour. Gold anomalies, up to 1.2 g/t , occur in rocks having BMS, or close to such rocks. The presence of abundant spinel and BMS at the base of the drill core may explain the high values of Rh and Au, along with Pt and Pd.

A genetic link between the presence of Pt and Pd anomalies and that of gold. may be supposed based on the mineralogical expression of the noble metals. Native gold may be included in sperrylite and palladiferous minerals may carry gold (up to 5.6 wt. Yo) at Lavatrafo. Small alloy grain (= 1 pm) carrying Cu, Pd and Au (rozkovite?) occur in small cracks cutting altered pentlandite with other secondary minerals (awaruite). In this case Au but also PGE, more especially Pd, may be remobilized by hydrothermal fluids.

In the Bulqiza ophiolitic massif, hydrothermal gold deposits are known in the vicinity of Pt-Pd deposits, either in mande rocks and upper-Moho dunite, Or in the gabbroic crustal sequence. At Ceruja, Bulqiza massif, gold occurs in an arsenopyrite vein with a calcite-rich gangue cutting the serpentinized harzburgite (Anonyme, 1985: Ceni et al., 1985). These hydrothermal deposits may indicate that remobilization of noble metals occurred (Helgeson and Garrel, 1968; Seward, 1984; Picot and Marcoux. 1988; Leblanc and Fischer, 1990; Sillitoe, 1991).

The contemporaneous presence of magmatic or hydrothermal PGE and gold mineralization is more and more underlined in basic -ultrabasic complexes (B arnes and Francis, 1995; Mernagh et al., 1994).

Precious-Metal Mineralogy

Madagascar target

Table 1- PGM identified in Andohankiranomena

		(N$_0$},~)
Laurite	RUS2	9
Eriichmanite	0ss2	1
Irarsite	IrAsS	5
Hollingworthite	RhAsS	3
Sperrylite	PtAs2	31
Guanglinite	Pd3(As, Sb)	1
Palladoarsenide	[(Pt,Pd]2As]	1
Pd-oxydes	PdOx	4
PdS		1

The proportion and size of PGM found in Andohankiranomena samples is compatible with the PGE pattern observed (table 1). The main Pt carrier is sperry,l i re (3-25 ~m) which predominates over all the other mineral phases (Fig. 10). Launte and erlichmanite are usually found in chromite grain with base metal sulphides. They she\\ the common Ru-OS substitution with significant proportion of Ir and Rh. Most of the other minerals are found with secondary silicates, hydrosilicates (Fig. 10). Because of the

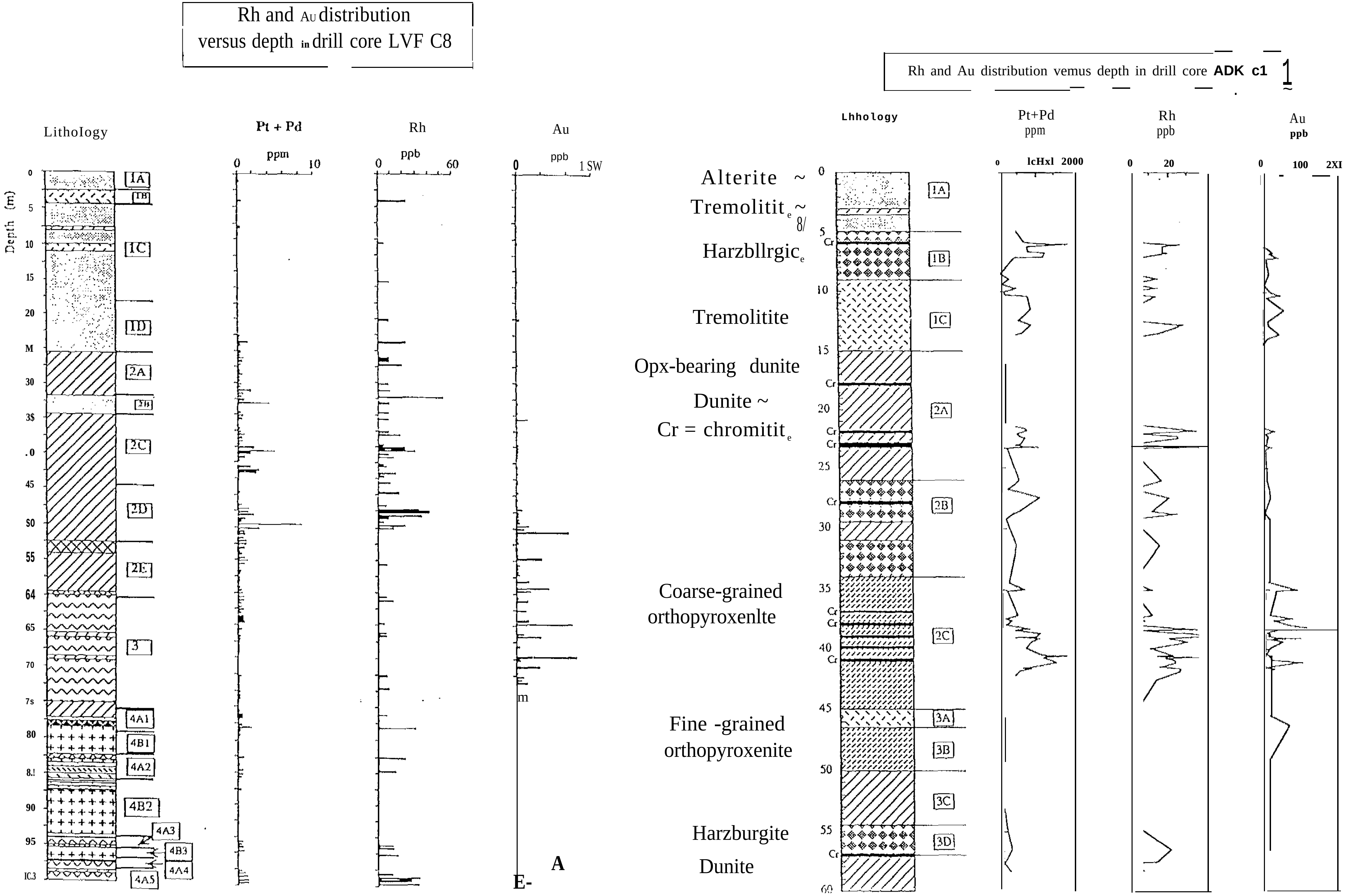


Fig 9 A and B, Pt+Pd, k and Au distribution versus depth in drill co LVF C8 and ADK

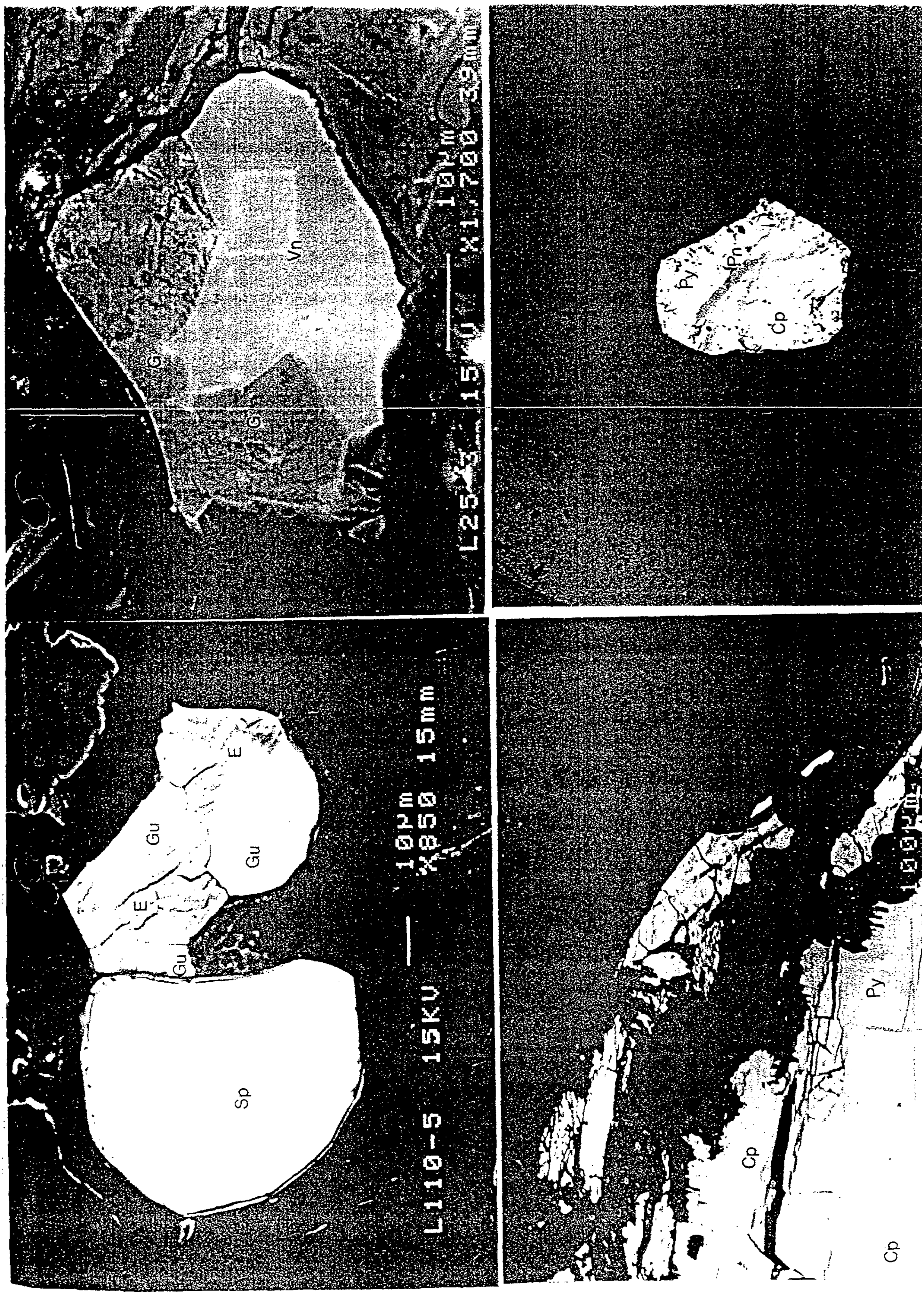


Fig. 10, PGM Assemblage in Madagascar targets. Sp = Sperry Ii[e; Gu = guanglinite: Vn =

hydrothermal alteration of rocks and weathering processes, it is often difficult to define the original setting of the PGM grain with respect to BMS and rnagmatic silic~tes. However, sperrylite which is locally found between large knots of pseudomorphosecl pyroxene phenocrysts, suggests that the PGM might have been located interstitially. between former pyroxenes and spinels, but this is difficult to confirm. h-arsi te and hollingworthite occur in association with sperrylite. Pal-bearing phases are found within hydrosilicates (MacDonald et aI., 1995),

Table 2- PGM identified in Lavatrafo

	(Nob,)	
Irarsite	IrAsS	2
Hollingworthite	RhAsS	
SperryIite	PtAs2	19
Palladoarsenide	[(Pt,Pd)2As]	2
Vincentite	Pd3(Sb, As)	6
Guanglinite	Pd3(As, Sb)	4
Unknown	[(Pal, Fe$_{j}$CU)21 (As S)5]	2
Mic'nenerite	PdBiTe	2
Palladium telluride		1
Unknown	[(Pal, CU)9(ASS)2]	1
Unknown	[(Pal, CU)13AS2]	
Unknown	[(Pal, Ni)12As 11]	

As for the Andohankiranomena intrusion, sperrylite is the dominant Pt carrier at Lavatrafo but Pd is present in a number of different phases, in sulfoarsenides rich in **Cli** and/or Ni, arsenides, antimonides and tellurides (Table 2).

Sperrylite is most commonly present as euhedral to subhedral crystals msociated with interstitial base metal sulphides (BMS), which may or may not have suffered secondary alteration. Subhedral to anhedral sperrylite is also found in intersti~ial areas entirely surrounded by serpentine and/or Fe-rich carbonate. One sperrylite was found with a rim of anhedral hollingworthite. B oth grains are included in serpentine.

Recognized Pd minerals include guanglinite, vincentite, palladoarsenide'? michenerite and possibly kotulsite, The presence of michenerite and possibly kotulsite where they appear as anhedral rims around pyrrhotite and also alone (between crystals of tremolite) is important in that these phases are often associated with hydrothermal Pd(re)mobilization (Watkinson and Melling, 1992).

Both in Andohankiranomena and Lavatrafo, Pal-phases are altered and (possibly remobilized). Sperrylite seems to have been the PGM which was most resistant to later fluid-driven overprinting. Several Pd phases appear very spongy in polished section anct give a consistently low analysis total. The low totals may suggest the presence of an element which cannot be detected using EDS. A hypothetical conversion of euch one of the elements in these phases to oxides produces totals closer to 10070. suggesting rhar oxygen may be the missing element and that the minerals may have formed via the oxidation of an earlier (higher temperature) phase. All of these Pd phases are in con[ac(with serpentine and goethite and this may imply a link between iow temperature (<500 "C] fluids and aiteration and oxidation of the PGM, The original composition most likely contained some Ru, Rh and Ir along with Pd in the structure. The presence of oxides m a weathering product have been recognized in Iateritic formations above mafic-ultramafic complexes (Auge and Legendre, 1994).

Albania target

.AI1oys constitute 73 **?10** of the minerals observed in Pt-mineralized rocks of the Tropoja deposit, sulphides 21 %, and other mixed rnineraIs (sulfoarsenides, arsenides, [e 11 uricies]. 6 % in the 34 rocks examined (Table 3). The real proportion is probably higher if the size

Table 3- MGM cmnpxi[iou or minerxls Ir.rund in Ihe Tropoja **rwf d it] htMvy** concentr:~tes

Mineral	Heavy concentrate	In situ mineralization	Nobs. (h.c.)	(in
Os-k- alloys	%,65 -o,zlro,lz-o,65 Ruo,lo. opto,02..oRho,o3-o	o~,68.0,26[ro,< 2.0,65RUo,$_1$2.0,03 p@,~.o,Q2ffho,o2.o		(lo
isof erropiatinum	pt2,g.2Rho,06Pdo,05Ruo, ol(Feo,87CUo,06)	Pt2,75Rho,l 5Pdo,05Ruo,021ro,020so,ol (i%O,gOcUO.0gNi0,02)	(42)	(13
Tetraferroplatinum	Ptl,02Rho,ol Pdo,oJFeo,6g@o,23Nio, ol)	Pto,g5Rho,05Pdo,03 (Feo,6rjCuo,20htio,09)	(13)	(11
Ni+ich teiraferroplatinum	Ptl ,ozPdo+oz(Feo.qaCuo.33 f40,1 3.)	Pto,88Pdo,o-#?ho,ol (Feo,60Cuo,07Nio,40)	{5)	(2)
Pd+ch tetraferropletinum	Pto,g7 Pdo,17Rho,ol (Feo,5gCuo,35)	Pto,81Pdo,20Rho,04 (Feo,w@0,30Ni0,04) _.	(2)	(4)
Rhodium equivalent of NXraferropiatinurn	Rho,golro,oaPta,02 Pdo,o~ **(Feo.uOo,o.iNio,o.d**	Rho,73Pto,241ro,ol Pdo,lo(Feo,73Cuo,l gNio,ol)	(2)	(2)
Tulameenite	(Pt2,05Rho,02Pdo,04)Feo,g3Cuo,g3Nioo2	(PI~,86ffho,02Pdo, jf)Fel,02Guo,S7Nio,lo	(11)	{19
Pd- richTulameenite		(Ptt,55Pdo,53Rho,og) Fel,~Cuo,7~Nio,09		(6)
~Fe,Pt) al{oys	Pto,57Pdo,ol Rho,ol Feo,25Cuo,16Nio,ol	Pto,6,2Pdo,03Rho,03 Ru0,01Feo,~7Cuo,03 Nio,02	(5)	(27
Pt-Cu-alloy	(P~,~~Pdo,04Cuo,~~Feo,2 $_1$Nio,o~)	(pto<78pdo,@CU2,88Feo.13 Nio,05	(1)	(6)
Laurhe	(Ruo,~6Rfro,2jO~,20iro,03P@,ol)Sl,83Aso, 75	(Ruo<goRhoio40~,l jiro,o+S2,@eo,o f	(13)	(50
Ertichmanite		(Oso,62ffuo,f2Rho,02 ko,21)Sl,~3A~,17		(1)
Cooperite		**(Pb,92pdo,03Rho,ol iro,ol)Sl,ozcuo,73Nio,og..**		(4)
Malanite		(Cul,ooFeo,o~)(P~,~~Rho,r#o,02)S4,01		(2)
Cu-rich Kashinite		([ro,82Cuo,52Ruo,2oFeo,ogRho,3oP~,ogFeo,o8Nio,o~)S~,o~		(1)
Holiingworthite	(Rho,620a&ogRuo,13ko,15PQ,olNio,ol)A~,66Sl,24	(Rho,620so,ogRuo,13ho,15P~,olNio,ol)Aso,6&~,~4	(16)	(7)
Sperrytite		(Pto,g4Rho,olNio,o l) Asl,g7So,06		(4)
Anduoite		(Ru0,790s0,1 lFtho,041ro,ol P@,olPdo,olNio,04)Asl ,g,gSo,ol		(1)
Pd -arsenide+lluride	(Pd.2,g4Pto,03Nio,o~Cuo,02)2Aso,g3Teo,g6Sbo,04	(Pd2,~l Feo,03.Cuo,ol)Te~,04	(3)	(3)
Rh-arsenide		(P,ht,lrjPdo,8~Pt&olNio,52Cuo,3&,Ast,02Teo,03		(1)
Rh-!e[luride		(Rho,73Pdo,14PQ,o lCuo,~3Nio,ol)Teo, ~6iigo,02		(3)

Table 4- PGtvl identified in Tropoja Reef

Rock sample	103A4	M78/10	35A5	92A4	60A5	2 3	59A9	89A2	M78 10	39A1	B2 2	M78/5	96A3a	92A5a	158A14	58A12b	58A13	58A14	90A9	158A2	158A4	58A11	157A15	69A8	157A7	157A9	60A3	B5/4	B5/1A	B10 6	B7 3	157A3	157A2	157A11	33A2
Pt31?e		X	x	x	x	x	x	x	x	x	x	x	x	x	x	x																			
PtFe		X							x			x	X	X								X			X	X	X								
(Pt,Fe)															X			xx	x		X				x			X	x	x	x				
P&													x	x																					
RhFe									X			X						X	X	X		X		X					X						
(Rh,Fe)																					x														
=2FeCu												X	x	x	x	x	x	x		X	x	x	x	x	x										
(Ptcu)																	xx	x		X						X						X			
(Pd,Cu)									x			x						X	X	X		x		xx	x										
0 s			X	X	X																														
RUS2	C	X			X	x	x	x	x		x		x																						
!?1s											x																xx	x			X		X	X	
@, Rh,P[)2s3						x				x																				X			X	X	
Cu(Pt, Rh)2S4																		X																X	
CuFeS2																																		X	
Cu5FeS4																																		A	
(Fe, Ni)9S8																		X		“															
RhAsS															x	x		X	X					X										X	X
tAs2																																			S
uAs2																																			
h3As																																			

of the minerals is considered. Grain size of alloys may reach 60 ,um, whereas the size of the other minerals are rarely above 10pm (Fig. 11 A).

About 95 % of the PGM are included in chromite, especially alloys (Fig. 11). There is a good correlation between the number of alloys found in a rock section and the Cr_z0_3 bulk-rock composition. This is compatible with a contemporaneous crystallization of PGM and chromite. Hence, a genetic relationships may be suspected between PGE mineralization and chromite deposits.

Pt-, Rh- and Fe- alloys represents 58 % of the alloys; other alloys are Cu-rich tulameenite and Pt-Cu alloys and Pd-Cu alloys. Laurite is the predominant sulphide (80 % of the total sulphides), followed by erlichmanite (8 ‘-%) and cooperite (6.5 %).

Three types of paragenetic assemblage maybe defined (Table 4).
(1) The first one is characterized by the association of isoferropiatinum, Iaurite. andlor Os-rich alloys. Cooperite was observed time and Ir_2Ss twice.
(2) The second assemblage is characterized by the association of isoferroplatinum and tularneenite. Compared to the first assemblage, laurite is only locally present. Other alloys such as tetraferroplatinum, PtCu and PdCu may occur, as well as hollingworthite.
(3) In the third assemblage, isoferroplatinum is not present. The predomin alloy is tulameenite, being associated with tetraferroplatinum and more frequently with Rh-Fe alloys, as well as with Pt-Cu and Pd-Cu alloys, the later Pt-, Pd- and CL]- beari n: alloys being well developed compared to the second assemblage. Hollingworthite is frequent; Rh-rich arsenide and malanite grains were observed only once.
(4) In the fourth assemblage, alloys are no longer present. A S-rich assemblage occurs, as indicated by the presence of cooperite with an $(Ir, Rh. Pt)_2Ss$ phase. associated in one case with chalcopyrite. Sulphides and arsenides are Pt-, Rh-, Pd- and Cu-rich. One sample is characterized by the presence of arsenides with cupmrhodsite.

When mixed assemblages occur, it may be noted that tetraferroplatinurn and tulameenite partly rim coarse grained isoferroplatinum associated with Iaurite and locally Os-rich alloys. The cooperite observed in the first assemblage ak.o rim isoferroplatinum. In the second type of paragenesis, coexisting isoferroplatinum and tularneenite are rimmed by Pt-Cu and Pd-Cu alloys and arsenide-rich phases.

The presence of cooperite around isoferroplatinum instead of Cu-Fe-Pt and PI-FM alloys representative of the second and third assemblage. The sulphide-rich paragenese of’ the fourth assemblage is characterized by the presence of cooperite and other Pt-Rh-lr sulphides indicative of high sulphur fugacity, Hence, the fouth assemblage may represent crystallization products of melt coexisting with isoferroplatinum of the first assemblage. This melt was enriched in Rh and Cu according to the phase composition. This is also compatible with the behaviour of Rh and Cu in isoferroplatinum which show a coupled increase at the expense of Pt.

High Rh content in the melt coupled with high Cu content do not correspond to experimental results showing either a low-Rh Pt_3Fe and PtFe association coexit in: ~!:i [h a 1ow-R11, high **Cli** melt, or a Rh-rich Pt alloys and Rh alloys associated with a Rh-rich melt (at least 20 at. To Rh) (Makovicky et al., this study). Moreover, the application of the experimental Pt-Rh-Fe-Cu-S system to the Tropoja low sulphide assemblage is biaisecl because of the presence of As andor Te in the natural system. In the Tropoja deposit. i [seems that Pt-alloys are associated either with S-rich assemblage or }vith an As-rich assemblage.

Considering the high proportion of sulphide with respect to arsenide and [el [uride. one may also suggest that a Cu-Fe based suluhide melt occurred, from ~~”hich Pt. anti iol Rh should have ~~en separated. Pt may be dfisolved in a Cu-Fe-S melt at high S fu:aeity (Makovicky et al., 1988). In the first type of assemblage from Tropoja. substantial amounts of Rh in the sulphide melt was indicated by the presence of PtS. [II-. FM. Pt 1~.s:.

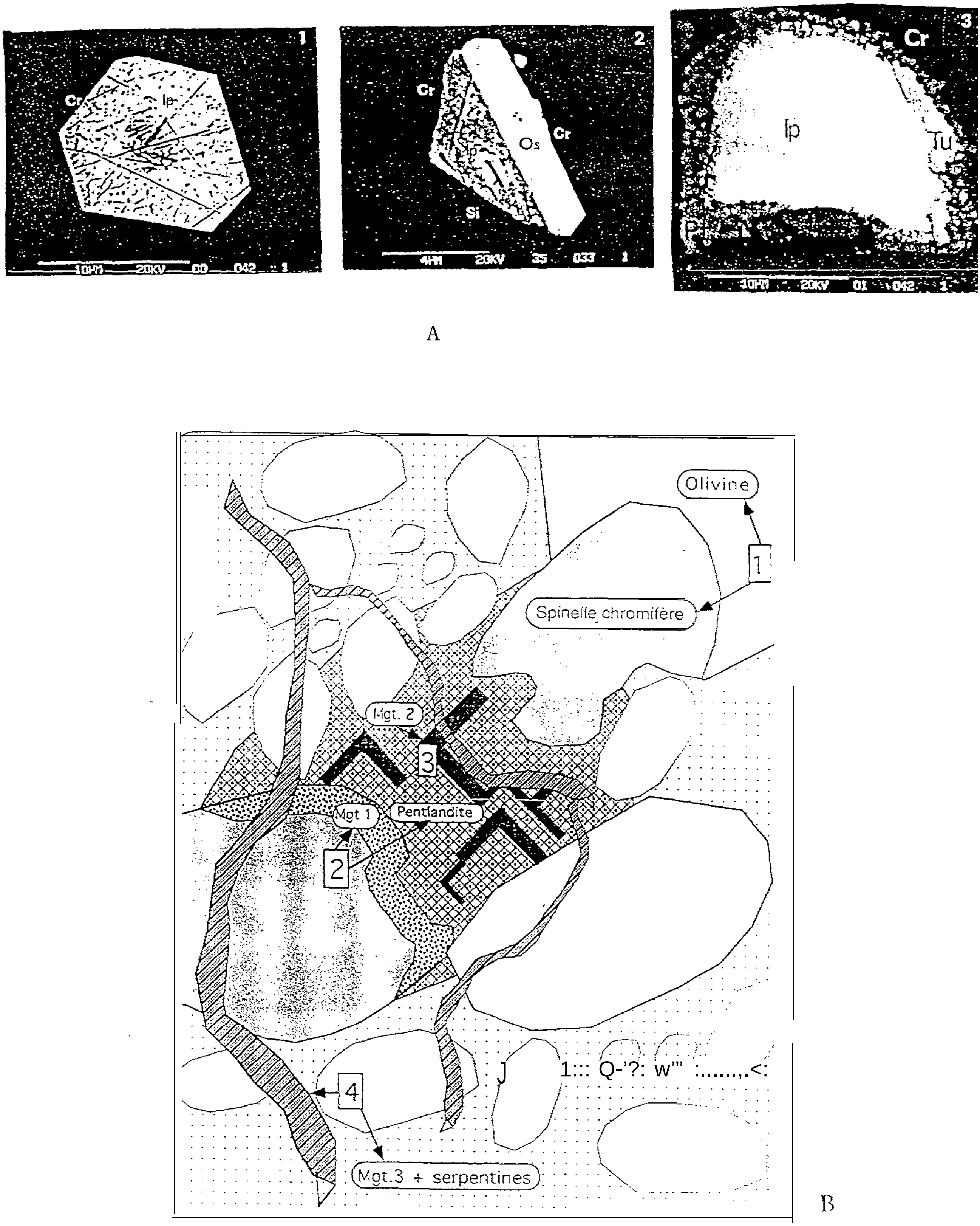


Fig. 11 A. 1) Pt_3 Fe alloy (Ip) hosted by chromite (Cr); 2) Pt_3 Fe alloy (Ip) associated with osmium (Os) and a silicate (Si) hosted by chromite (Cr); 3) Pt_3 Fe alloy (Ip) associated with tulameenite (Tu) and a silicate (Si) hosted by chromite (Cr); B. Successive mineral assemblage observed at) Bulquiza.

:~[~<i [Ili(wpinc[s <Rudashevskii et al., 1985), indicative of a high sulfur fugacity. For the s~lcc~[d :~nd (Ilird [ype of assemblage, it may be proposed that a substantial amount of Rh (:IIKI (’II) wm separated from the sulphur-rich melt. The residual nature of the sulphide II ICI(iil”tcr cx[raction of Pt and Ri-i, entering the three assemblages, is also attested by [he cllrich[]wnt of Pd and ATi, besides Cu, and the residual Rh, Pt, and other PGE in the melt, ‘ I’IWSC clcnwn[.s would later form the minerals of the fourth assemblage. A Pt/Fe decrease is {d}scrvcd in [he successive crystallizing Pt-Fe alloys.

The assemblages described at Tropoja indicate that these was probably a differen[sulphLlr fu:ocity in the ore fluids. Low S fugacity is expected during crystallization of [~(>[ls[~~cltic>tl~ctric Pt_3Fe, and other Pt-Fe alloys. Rims of Rh-rich alloys arouncl is{) [“c rmpla(i nL] m (second assemblage) would indicate lower sulphur fugacit ies than for awwia[ions of P[$_3$Fe rimmed by cooperite.

Distinct PGM assemblages are usually found along Pt-reefs from cornplexe> ~vorldwide. In Tropoja, the setting of chrornitite hosting the PGE-mineralization in cl~kes is probably responsible for distinct conditions of fS2 deduced from the composition of the zoned mineral assemblages.

The mineral assemblages described at Tropoja were also found in heavy all u\’i LI m concentrates from the eastern Albanian ophiolitic belt. Another interesting feature in hea>v al I uvium concentrates is the presence of Os-Ir-Ru alloys of variable composit i on. S om> of them are associated with isoferroplatinum.

The association of(1) L--rich isoferroplatinum (Ir up to 6 at.%) with other [r-OS-**RLI** alloys and irarsite as well as (2) the association of isoferroplatinum with Pt- and Rh-rich osmiridium (Pt up to 5 at.%; Rh up to 2 at, %), and rutheniridosmine (Rh up to 3.5 at .7~: Pt up to 3 at. $%, and Pd up to 2 at.%) observed in the alluvial concentrates differ fi”om the Tropoja-type mineralization. In the first case, the presence of high Ir content in isoferroplatinum, associated with irarsite and Ir-Os-Ru alloys, is distinct from the Tropoja assemblage with Ir-poor isoferroplatinum, Ir-bearing sulphides and laurite.

Both nugget association would indicate a Pt- mineralization associated ~t irh iridium group PGE (IPGE). Such mineralization should have a lower (Pt+Pd+Rh h’I Ru - Os-Ir) ratio compared to the Tropoja mineralization because of the close association of Os-Ir-Ru aHoys and isoferroplatinum. Only some Pt-mineralized mantle-chi-omitite from 13ulqiza have a PGE distribution compatible with a mineralogical association carr>’in: IPGE and Pt. There, the Pt content is variable for a quite high Pt/Pd ratio (1 < Pt/Pcl <5 } and the IPGE and more specifically the Ir content may be quite high (= 1 pprn), However, PGM from this type of deposit are composed of Ir-rich laurite with secondar! PGE-alloys, and sulpharsenides. No isoferroplatinum was observed; Pt, Ir and to a le.<se r Sxtent Rh and Pd are carried by arsenides and sulpharsenides (irarsite, sperryli te) ~ Kar;Ij. 1992).

The palladiferous Bulqiza mineralization is characterized by the presence of pentlandite and smaH rare PGM. Other minerals are millerite, violm-i[e. awami~e. ~magnetite and rare pyrrhotite. Secondary Au- and PGE- bearing alloys ailcl lo~v temperature PGM (Pd-Bi phases) occur in smalI cracks cutting pentlandi[e (Fig. 11 B}. The origin of the Bulqiza rnineralization is relevant to the Pd-Fe-Ni-S system (Mako\ick: and Karup-Moller, 1995).

Base metal sulphides (BMS)

They are locally well developed in one Lavatrafo intrusive and in the Bulq iza target. At Lavatrafo, base-metal sulphides from drill core LVF C8 (Annex 15) were studied first because of their size and abundance. They are composed of pyrrhotite. pentlandite and chalcopyrite. In Andohankiranomena, BMS are rare and occLw as inclusions in chromite. The content of Pt in pentlandite may reach 1.1 w't/70 in one sulphide bleb.

The pentlandites show no regular chemical variation with depth. They have a Fe/Ni ratio of about 1, and are enriched in cobalt (0.91< Co <1.38), but Co shows no significant variation with depth (Fig. 2.2. 1). They also locally contain significant amounts of Cu (up to 1 wt%) and traces of Pt (up to 0.08 wt%) and Pd (up to 0.27 wt 70). These trace element contents are close to the detection limit obtained with the microprobe (0,02-0.08 wt~o).

The chalcopyrites all contain substantial traces of As (up to 0.05 wt% }. B i (Lip to 0.08 wt%) and Ni (up to 0.41 wt%).

In the pyrrhotites, the Fe/S ratio decreases towards the lower part of the ch-ill core. Cu (up to 0,06 wt~o), As (up to 0.06 wt%) and Bi (up to 0.09 wt'?io) are present as traces. Ni is often detected and can reach 2.68 wt%.

Many of the intercumulus sulphides in the LFV C8 core have been extensively altered by secondary fluids associated with serpentinization. The sulphides react in the general sequence: pyrrhotite > pentlandite > chalcopyrite, and it is not uncommon to observe >90$Z0 replacement of the Fe-Ni-Cu sulphides in some samples. The replacement minerals are a complex mixture of serpentine, goethite (FeO.OH) and Fe-rich carbonate. and the process of replacement appears to take place preferentially along sulphide cleavage planes.

Based on the order of appearance of the minerals, some PGM clearly crystallized later than the BMS and this is illustrated by the inclusions of BMS in .sperrylites. However, other clusters of PGM and BMS indicate that their growth was contemporaneous. The PGM have more euhedral - subhedral forms than many of the sulphide minerals, and the outlines of the PGM clearly follow the outlines of rhe larger ~?olume of Su]phide, This would appear to indicate that the PGM crystallized first from the early sulphide solid solution and that most of the PGE, As and Sb partitioned into these phases. Crystallization of pyrrhotite, pentlandite and chalcopyrite in these cases took place after PGM crystallisation.

In Bulqiza, pentlandite is locally enriched in Pd (up to 0.5 wt. Yo). The Fe/Ni ratio of pentlandite shows slight variations from one site to another. Along the K-asra section. no Fe/Ni variation is observed with stratigraphy. However the Co content may 1 ocall y reach 13 wt.%.

Experimental results

Phase systems that correspond to the associations observed in low-sulphur PGE deposits are experimentally very demanding, Experimentation with S-free s>stems did not yield usable results even at temperatures as high as 1100"C. It turned out thiit the best "fluxing agent" is sulphur and, as a consequence, the systems were investigated usins low-su]phur, metal-rich charges. For all phases which do not incorporate SLIlphLIr. the compositions and phase relationships remain practical y unchanged. whereas reactivity and equilibration is substantially improved.

l'li~tinu]ll-i~~n alioys are the fundamental ingredient of PGE mineralization poor in Ii MS. Tlw firs[system investigated was Pt-Ir-Fe-S, and the related subsystem lr-Fe-S. I] L-L'; ILISC of low reactivity, only isothermal studies at 1000"C and 1100GC could be c.(}[llplc(cd in [he first case, 800"C was added in the second case. There are a number of spcci I'ical [y "Pt-lr type" low-sulphur PGE occurrences in the world, e.g. in New South **Willts (Jol]iill** et al. 1990) or in E Siberia (Mochalov 1994) for which this system is i ll~p~~rt ant. As it happens, the Madagascar and Albanian deposits, except for the Albanian :tlluvium concentrates, all turned out to be of another, "Pt-Rh" type and our results are n(~[dircc[]y relevant to them,

-1-lt(' plmt' Syts'felll *Pt-Ii"-Fe-s*

The Pt-Fe-h--S system (Fig. 12) is a good geothermometer for the second stage of OW formation defined here, in-the "ore d-epos;ts of the Pt-Ir association. Its ;Iloy compositions in the Pt-richer half' of the system are sensitive indicators of temperature. **i~]ld** their overall composition also of S fugacity. For the ore fluids, it yields a sequence ~v]]icll corresponds to

(a) very low- (such as in Fe rich melt),
(b) intermediate- (pyrrhotite compositions), and
(c) high (Pt-rich sulphide melt, PtS, thiospinel) sulphur fugacity.

A disadvantage is that a number of intermediate to high fugacity asselmblages contain close-to-stoichiometric Pt3Fe as a component, with low Ir values. These Pt3Fe compositions are so close to each other that their separation is not possible in practice. Still, our results bring substantial re-evaluation of temperatures determined previously by extrapolations from the pure Ir-Pt system.

Comparison of our investigations with natural data suggests a hypothesis: looking at the Pt-Ir solubility values in synthetic runs and the Ir values observed in natural Pt-Fe alloys and, vice versa, at the Pt values in natural Ir-Fe (-0s etc.) alloys, we believe that the majority of Ir (0s) phases in iron-platinum alloys (and vice versa) may be products of fluid-assisted exsolution from original solid solutions at higher temperatures. This was suggested by Johan et al. (1989, 1990) for some texturally obvious cases, although they did not try to analyse the total alloy compositions before exsolution, in order to attempt to approximate the original temperatures, We think that this phenomenon may be much more widespread than admitted. This would agree well with the fluid-driven multi -stage mineralization process suggested by field data.

The phase sysrent Fe (Cu) Pt-Rh-S

The Rh-Fe-S system (Fig. 13) is very relevant to the examined low-S ore deposits. In order to enhance reactivity, and because of the role of Cu in the known PGE deposits which are low in BMS, Cu was added to the system in the ratio Fe:Cu =4: i.

The synthetic Pt-Fe-Rh alloys contain little Cu, tulameenite [pt$_2$Fecu} 11:1s not been observed; Cu contents in alloys increase somewhat from 1000^C to 1 100"C. SoIubility of Rh in iron-platinum alloys is high, much higher than for Ir and it appears not to be sensitive to temperature in the range 1000- 1100"C. Reactivity Pt-Rh is poor anti no usable data could be obtained under 1000"C. Volubility of Pt in Rh-Fe alloys is [modest; the phases obtained in the system were found by our colleagues in the Tropo~a deposit, e.g. they decribed the same gap between RhFe and a rhodian P[Fe found by Lls.

Pt-Rl-i-Fe alloys coexist with two immiscible types of sulphide **melt.** Low-Rh Pt~ Fe and PtFe (and Rh-poorer u-RhFe) coexist with a low-Rh, high-Cu melt whereas [he Rh-rich Pt alloys and Rh alloys associate with Rh-rich melt (at least 20 ar. ToRh in

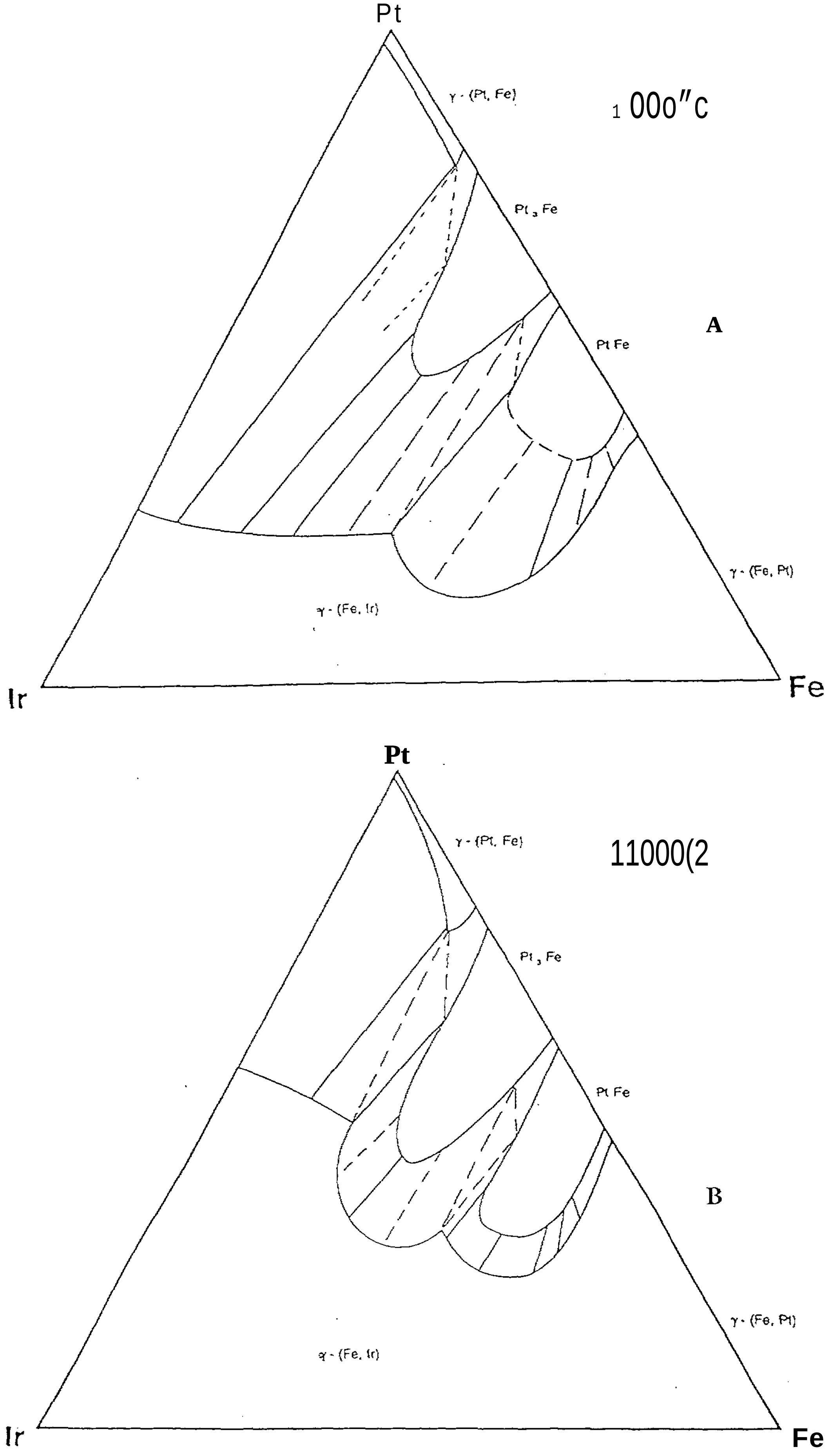


Fig. **12** Phases and phase relations in the system Fe-Ir-Pt at 1000”C, 12 **A** and AT 1L00″C.
12 II in the presence of sulphides.

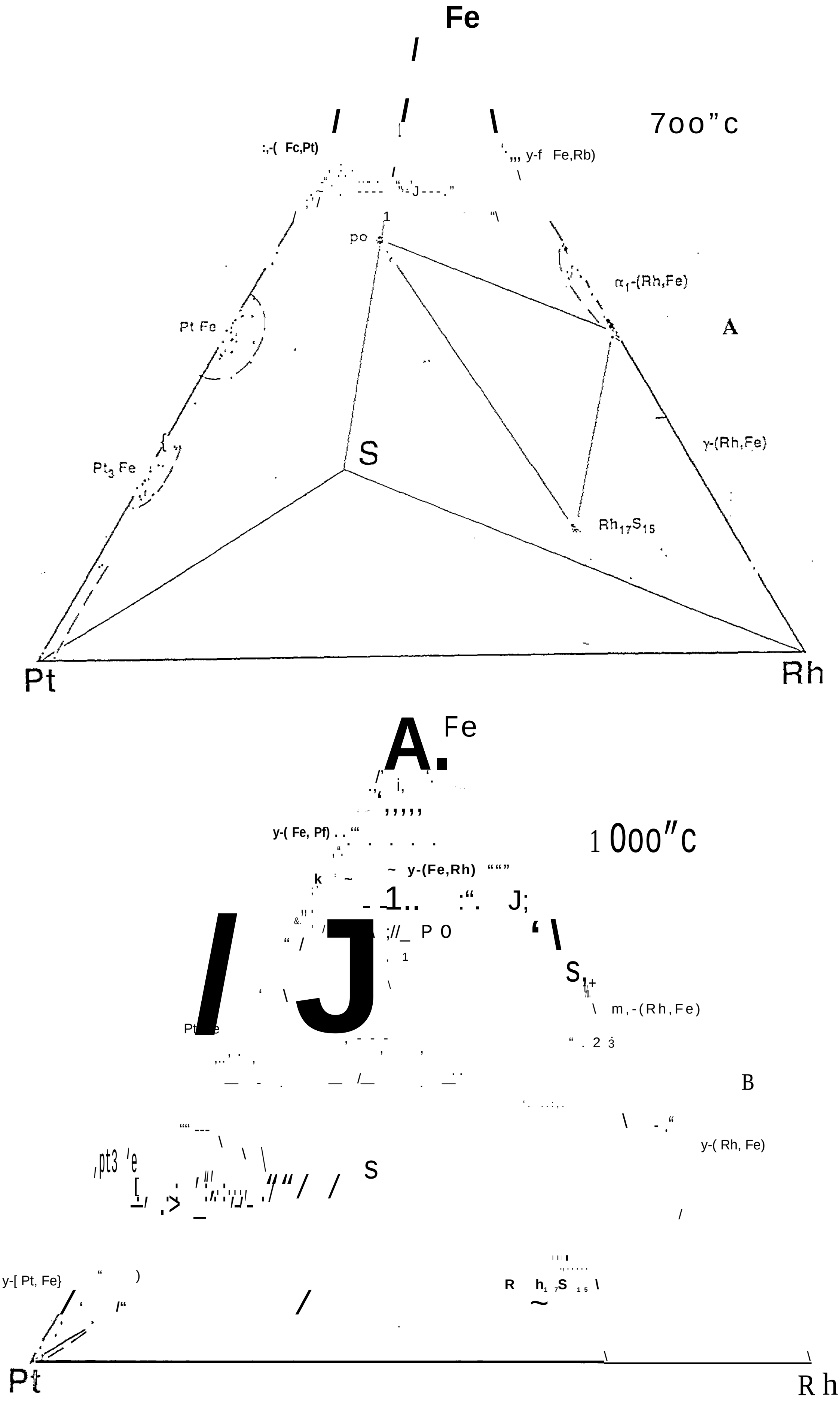
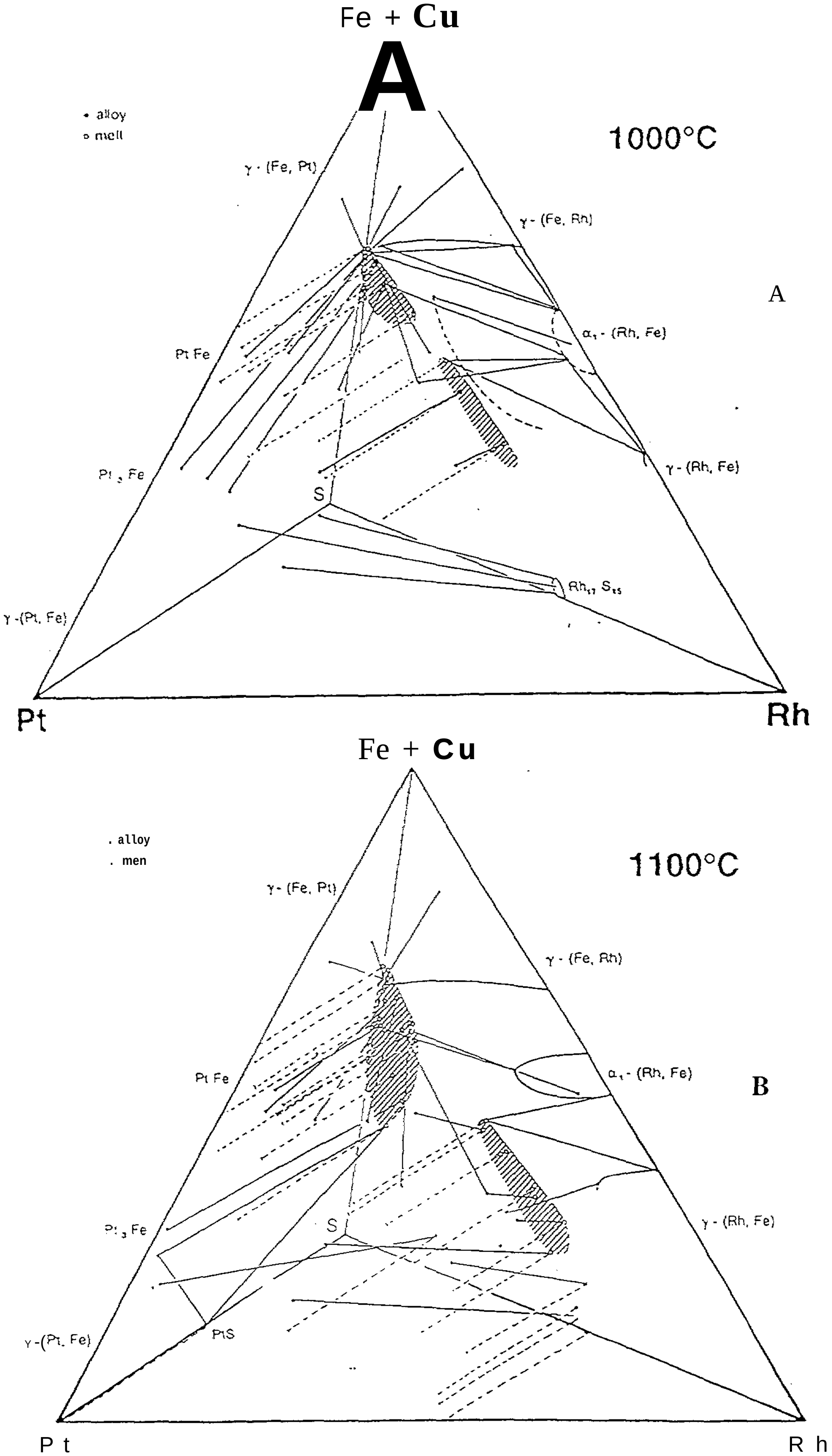


Fig. 13, Alloy compositions and associated phases k the Pt-Rh-Fe-S system at **700"C.** 13 A and a[10OO°C, 1313.



~ig. 14, **Immjscjbl~** su]ph& melts (~led) and the `coexisting` pt-Fe(~u)-Rh alloys (front face oulined only in part) in the phase system Pt-RhFe+Cu-S at 1000”C, A and 1100”C, B.

melt). N'aLLlra[phasus qLNNcd in this report suggest that both tjfpes of associations are potential] y prcsc[lt in [hc deposit, crystallization products of such melts are recognized in the sulphide-rich liwrlh msemblage.

The CH-FC hascd sulphide melts are strong PGE separation agents in their presence, Pt SINN[Id cssent ii.dly be separated out of the sulphide portion and concentrated into Pt alloys wlwwas substantial amounts of Rh should be capable of moving on, together with lhc sulphide component, and crystallizing separately.

The parlia[Cu-Rh-S system (Fig. 14) serves as a sulphur-fugacity indicator for Rh-containin: deposits, and also as a sensitive temperature indicator because of a spectrum of changes in phase relations between 900°C and 500”C. Four Rh-sulphides (CLI volubility in [hem does not change appreciably with temperature), alloys {memi solubilities change drastically with temperature), covellite and four ternary sulphides offer good possibilities to pinpoint both temperature and fugacity of equilibration in the deposit.

In the mixed tissemblage, instead of the thiospinel cuprorhodsite Cu~$^{+}$Rh3+2S$_{i}$ (known from a llLllllber of deposits), maIanite will form, approximately cu+pt~+ (Rhs+. Ir^{3+}, FeS+) S$_{J}$ as observed by us in the synthetic runs, Both indicate high-S fugacity. The Cu-containing IrS$_{z}$ in the natural material confirms this, suggesting that locally high sulphur fug,acity conditions developed even in the Iow-sulphur assemblages poor in 13 MS.

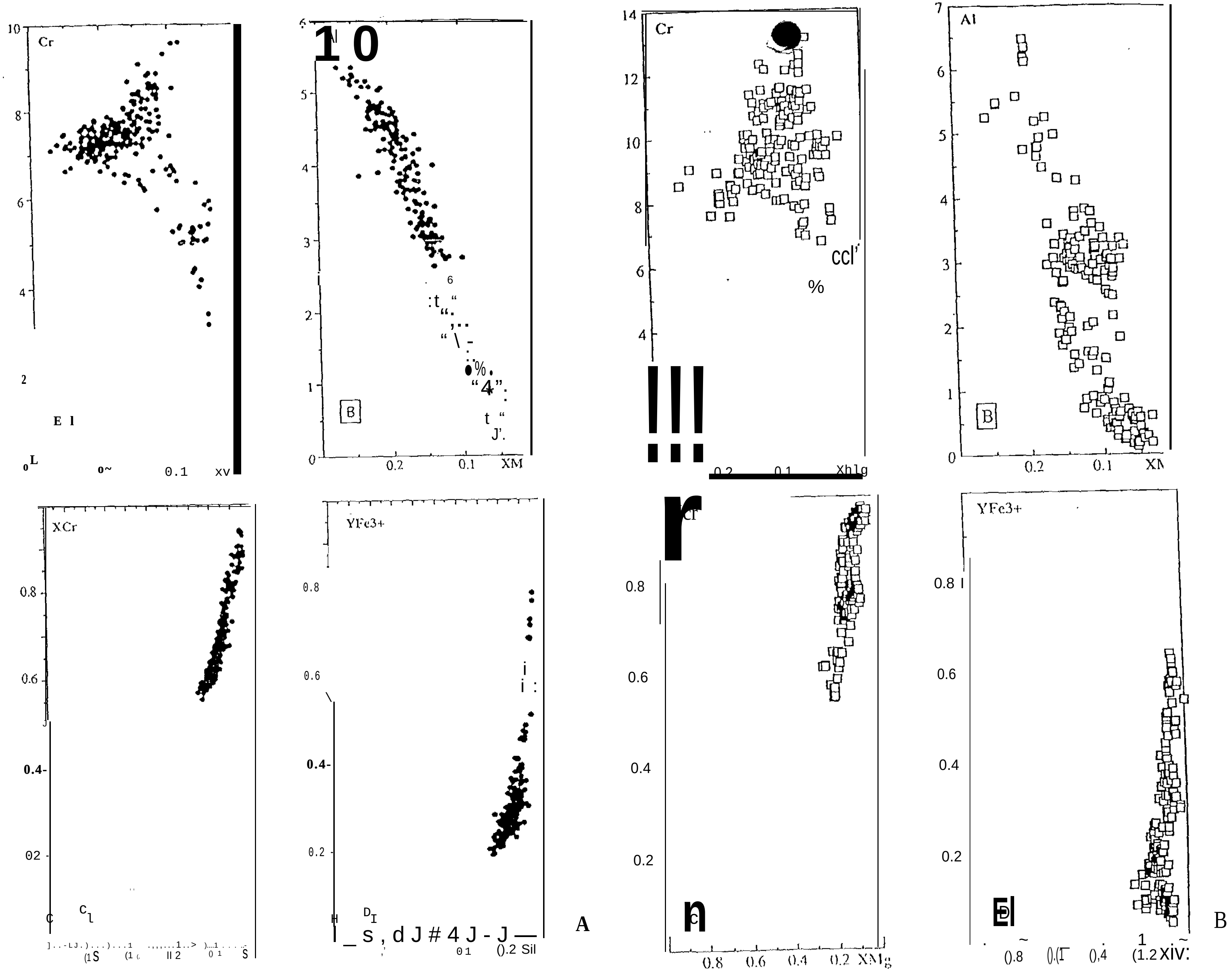
Chemical evolution of chrome spinel

Chrome spinel is an ubiquitous mineral in the mineralized horizons and the host rocks. The evolution of the mineral composition was recorded along sections from all the targets. The evo~ution of spinel composition is usually strong in all the studied targets.

Two evolutionary trends are observed for chromiferous spinels of the Lavatrafo and Andohankiranomena intrusions, when projected in a XCr versus XMg di ag-am: firstly, an increase of Cr content coupled with a decrease of XMg, and secondly a decrease of XCr coupled with the lowest XMg corresponding to ferrichromite formation during a serpentinization process (Fig, 15). The Cr enrichment of the first trend is coupled with a strong increase in Y Fe3+ [Y Fe3+ = Fe3+ / (Fe3+ + Cr + Al] and Ti and a decrease of Al. Such a trend is related to the magmatic evolution of spinels which however differs from that observed in layered complexes (Irvine and Findlay, 1972). Compared to Lavatrafo, the Andohankiranomena chrome spinels have a lower Y Fe~+ ratio and (Fe3^{+} + Ti) content, compatible with a crystallization under more reducing conditions, and higher ZnO (up to 1.17 Yo) and V$_{2}$0$_{3}$ (up to 0.79 To).

Other core-rim variations observed in spinels depends on the nature of the acljacen! minerals and is indicative of late magmatic reaction or subsolidus reaction. Fe~$^{+}$ and Cr enrichment towards the rim occurs in spinel close to serpentinized olivine. Such a trend is absent in spinel enclosed in fresh olivine. An unusual Fez+, Mg and Mn enrichment was observed towards a pyrrhotite crystal having Mg and Mn three times enriched compared (o spinel. Likewise, Ti content of spineI may increase towards the rim juxtaposed to an iImenite grain.

In Tropoja, spinels of Pt-mineralized rocks and adjacent barren rocks show a higher Fe^{3+} content compared to spineIs from the underlying mantle rocks. The Fe@$_{3}$ Viiriittion extends over several units of fO$_{z}$ on the logarithmic scale, indicative of lower f~$_{z}$ during the entrapment of Pt-alloys (Fig. 16A).



A and composition of Andohankiranomena

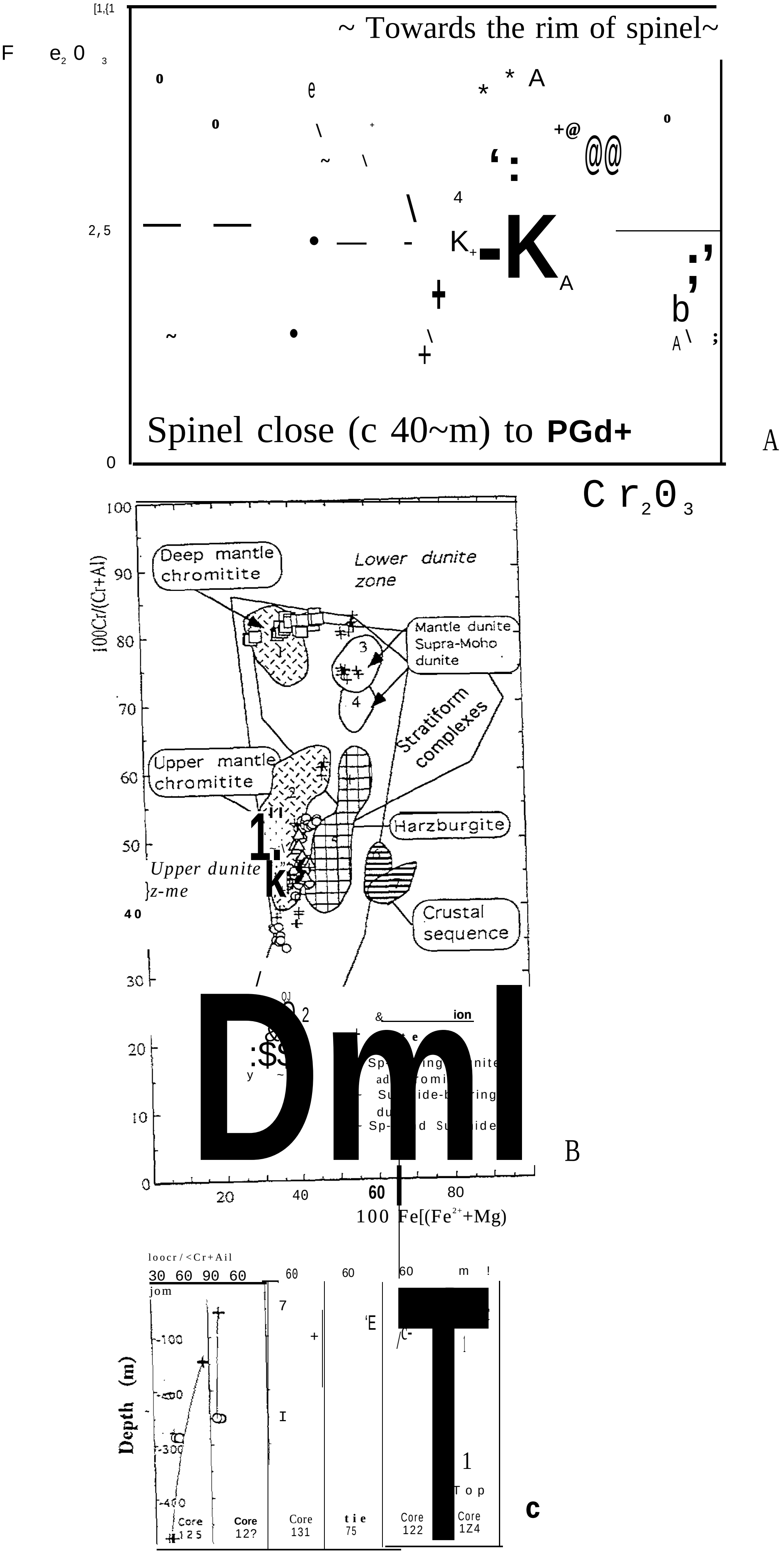


Fig. 16, Composition of-Albanian spinels. Variation of Fe_2O_3 vs Cr_2O_3 in spinel from the Tmpoja ophiolitic complex. Note the increase in Fe_2O_3 from the spinel close to the PGM towards the rim of the spinel grain, A. XCr vs XMg of Bulquiza spinels, E. Variation of the

In Btilqim. (ıw l’icld of spine] composition encompasses that observed both in the whole undcrlyin: l~litn[lc sequence and in the overlying cumulates (~ina 1985: 1987: Cina et al. 19861, k’lc[:lilurgic chromiferous spinels from the lower dunitic subzone show variation ~~i’ the XMg ra~io [XMG = 100*Mg / (Mg+Fe); 42< XMg< 7 1] for minor variation of [he XCr ratio [XCr = 100*Cr / (Cr+Al); 73< XCr< 83]. Contrasting evolution :ind conlpt>sition are recorded for chromiferous spinels of the upper dunitic subzone carrying 1 hc P(-mineralization. There, chromiferous spinels are refractory and their composition is controlled by variation of the spinel molecule [45< XMg< 67:34< XCr< 6 I]. The proportion of this molecule increases with stratigraphy (Fig. 16C). The spine] composi(ion of upper dunite is close to that of overlying gabbroic rocks. except for the XMg ra~io which is lower in gabbroic rocks.

Origin of the mineralizing system

REE and trace element distribution, and Sr and Nd isotope geochemistry

, The trace element analyses were carried out by instrumental neutron acti~ation analyses (IINAA) using two separate irradiations: one with total flux (10 ^{t5}n/s/cm^{z}) to determine Cr. La. Ce, Sm, Eu, Yb and Lu, and the other with epithermal neutrons {2. 1014 n/s/cm~) behind a Cd filter to determine the other elements, <Tb. Ir, etc.). This second irradiation method also enables us to verify the La, Ce, Sm. **ELI** and Yb concentrations.

Concentrations of incompatible elements (Th, U, Ta, Zr, Hf, Cs and Rb) are low for all of the dunites. The average Th/Ta ratio in dunites is 2.6 A 1.5 (1 o}. This low ratio, close to 2, indicates an extensional setting since we can consider that the Th/T’a ratio is not fractionated and is representative of the liquid in equilibrium with olivine from dunites, Most of the dunites have low Th contents (below or around 0.10 ppm}. When associated with a low Th content, low Cs and Rb contents indicate a limited contribution of continental crust, The most weathered sample (16) contains no more Th. Cs and Rb than other dunites. Because of the high metal contents of all of these samples. we ~vere unable to measure the low Sr contents.

The REE patterns obtained from the dunite of the Lavatrafo intrusion are very differen[from the patterns obtained from dunite of ophiolitic massifs. which are characterized by a V shape due to enrichment in La, Ce, and Yb, Lu with respect [o the intermediate REE (Sin, Eu and Gal), The REE patterns of the Lavatrafo dunire show I ittle HREE fractionation and an enrichment in LREE (Fig. 17). In addition, the assemblage is at a level 100 times greater than that of dunite from elsewhere (cf. Montigny. 1975: Prinzhofer and Alli2gre, 1985). As the ‘alterite’ (sample 16) REE fall exactly, in the same field as those from the little weathered dunite, the enrichment in light and lnternwciiate REE is not due to weathering. Therefore two hypotheses can be considered to account for the REE concentrations:

1) A direct contamination by only 1% crustal material, which would account for [he REE pattern of the Lavatrafo dunite without changing the overall chemical composition of the rock. Moreover, it is striking to note that the REE pattern of the ric best ciuni te sample (34) is very similar to that of present day crustal material.

2) A metasomatic fluid, even weakly enriched in incompatible elements. which **tf”OLIId** considerably modify the concentration of such dunitic material extremely poor in incompatible elements, Certain dunite from core LVF C7 (e.g. sample 277). t{hich is noticeably richer in REE, favours this hypothesis.

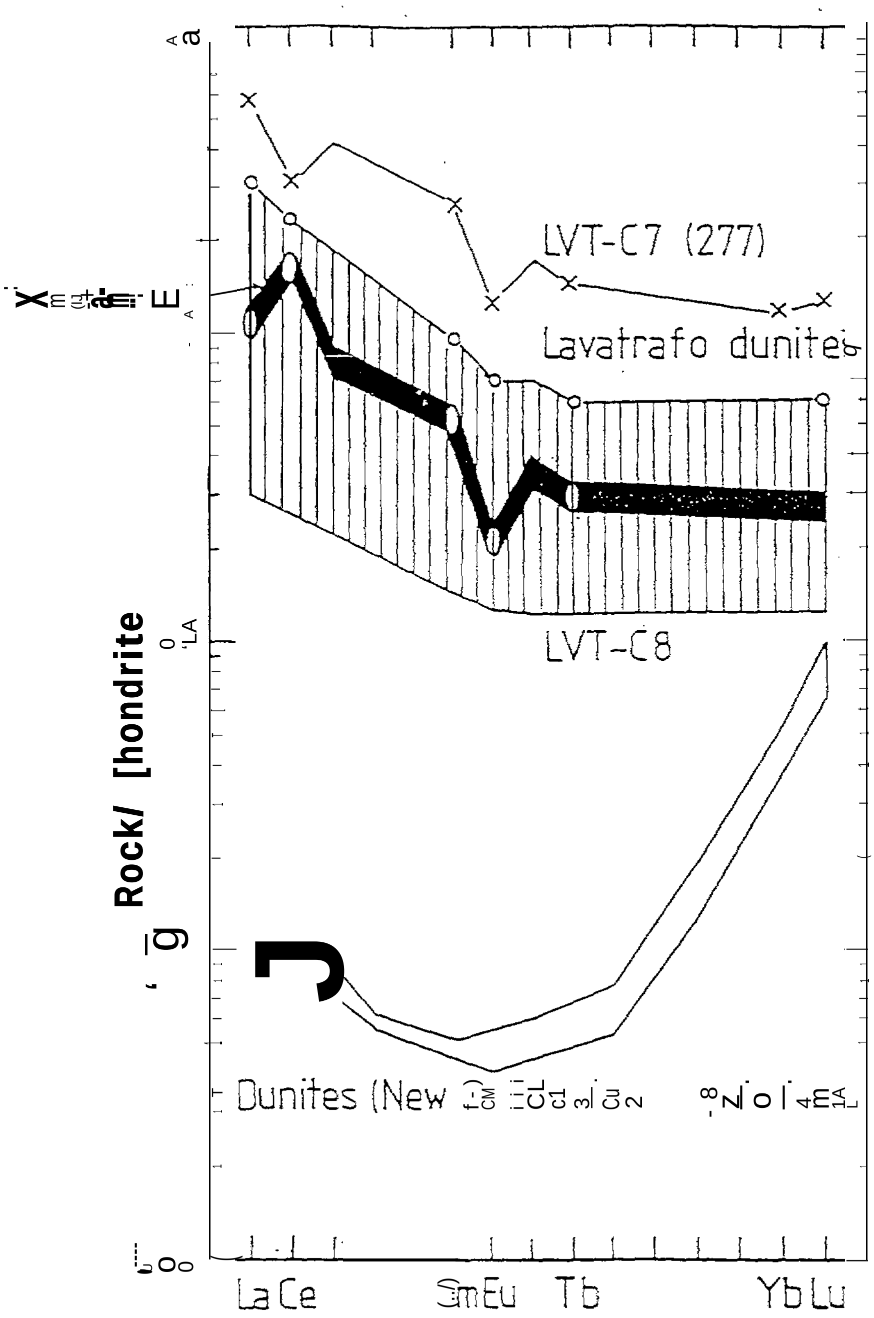


Fig. 17, Field pf REE Patterns from dunite of LVF C8 compared with those from ophiolitic dunite of New Caledonia (Prinzhofer and Allegre, 1985) and with the average pattern of highly weathered dunite (alterite).

AII is(~t<y]ic analysis was made on 14 samples from the Pt-barren Bemongikely []]:issi 1' (Al]~l~>l}:~llki ri~Ilolnena-type intrusion) and from the mineralized /\[]~[(~lt:l[~k il:~ll{~[l~cl~~~ and West Lavatrafo massifs. In the latter, samples were taken from Ixl[ll [Ilincral imd and barren facies and both with, or without, BMS.

Al I thu basic rocks studied gave very high Sr ratios (> 0.713). The ESr calculated t'~)r t [w ;ICC (>i' cm~~lticernent (790 Ma) gave very positive results (apart for sample 11 l) of hctwccn- + I ()() ~~~~d +420, which are ~ar hig~e; than the mantle value of **O.** The very pt~sit ivc E Sr rcllects a mdiogenic Sr contamination of the parent magma of the intrusions. The part icul M characteristics of sample 111 at the base of the drill core (high Rb content: Sr is<}topic ra[io of > 1; e Sr (T) >>0) remain, for the time being, unexplained.

The Nd isotopic geochemistry also indicates a very crustal character for the LI It rabasic magma (Fig. 18). The present c Nd values are highly negative and the Sm/Nd ratios reflect LREE-enriched spectra (apart from samples 12 and 25). The CN d (T = 790 Ma) are everywhere very strongly negative between -17 and -39. The model :Lzes. when they can be calculated, vary between 2.3 and 3.3 Ga and the E Nd (T) are. on tt~e ~vhole. very simi~ar (-17 to -23). The average value for the impoverished mantle of 790 Ma is around +6, Thus the position of both Nd and Sr in these rocks excludes a direct mantle derivation for the basic rocks and implies the inter}-ention of secondary processes. Either the parent magma of the intrusions was contarnina[ed by an assimilation of crust al rock, or the modifications in REE and in Nd and Sr isotopic compositions were caused by an intense metasomatism.

With the BemongikeIy and Andohankiranomena rnassifs. a massive cru.stal contamination (1570) would account for the LREE enrichment, but would also have caused an overall compositional change in the pyroxenite. A small amount of contamination by the ancient crust would impIy, for the contaminant, very high Nd contents as well as the very negative c NTd; characteristics that are in disagreement with the isotopic characters of the 'gran-ulite facies basement sample which has less negative a Nd (T) than some of the basic rocks. The metasomatic hypothesis appears more probable for these two massifs. The intervention of a fluid would explain a fairly high modification of the REE and the Nd and Sr isotopic ratios, whilst retaining the overall distribution of the major and minor elements.

Where the Lavatrafo intrusion is concerned, both hypotheses couId be valid. The Rb, Sr, Sm and Nd contents of the samples are very low compared to those of the crLlsml rocks. A weak contamination by an older basement would greatiy modify the isotopic characters and the REE spectra without affecting the overall composition of the sample. Similarly the intervention of a metasomatic fluid enriched in incompatible elements anti very negative in Nd and positive in Sr would give the same resuIt.

The stable oxygen isotopes, however (see Iater), impose certain con~tr:~in[s [h~~r make it possible to choose between the two possibilities. They indicate that (a) the contamination occurred at high temperature (T >450°C), (b) the contaminating crustal component was probably a fluid, and (c) this fluid intervened in a low water/rock ratio. This would favour the metasomatism hypothesis, with the fluids having acquired strong crustal characteristics when percolating through the basement, and being sLlfficient~y enriched to impose this isotopic signature on the basic magmas.

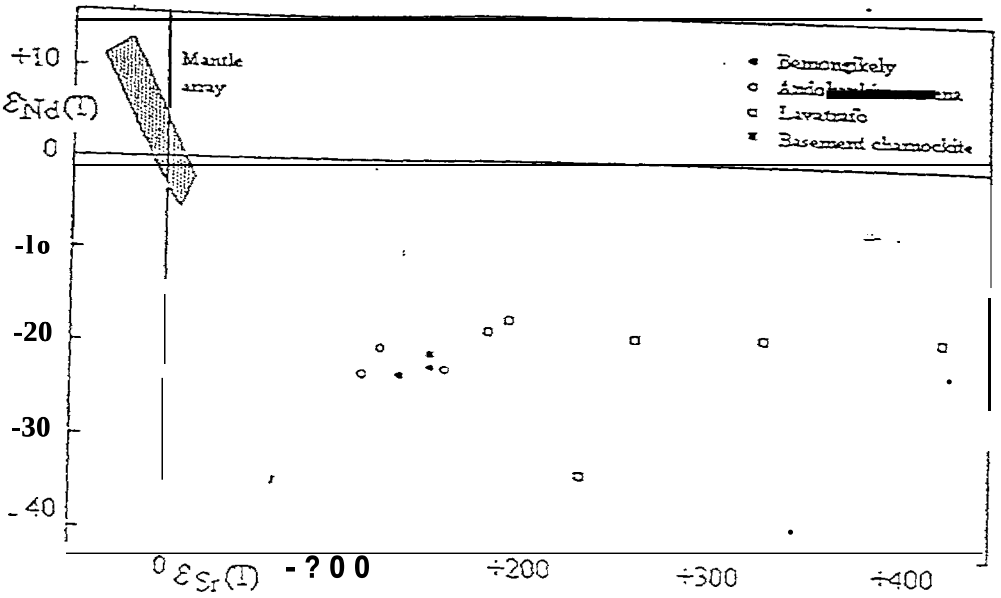


Fig. 18. $\varepsilon_{Nd}(T)$ VS $\varepsilon_{Sr}(T)$ diagram for the basic rocks and the basement charnockite. The mantle areray is shown for comparison.

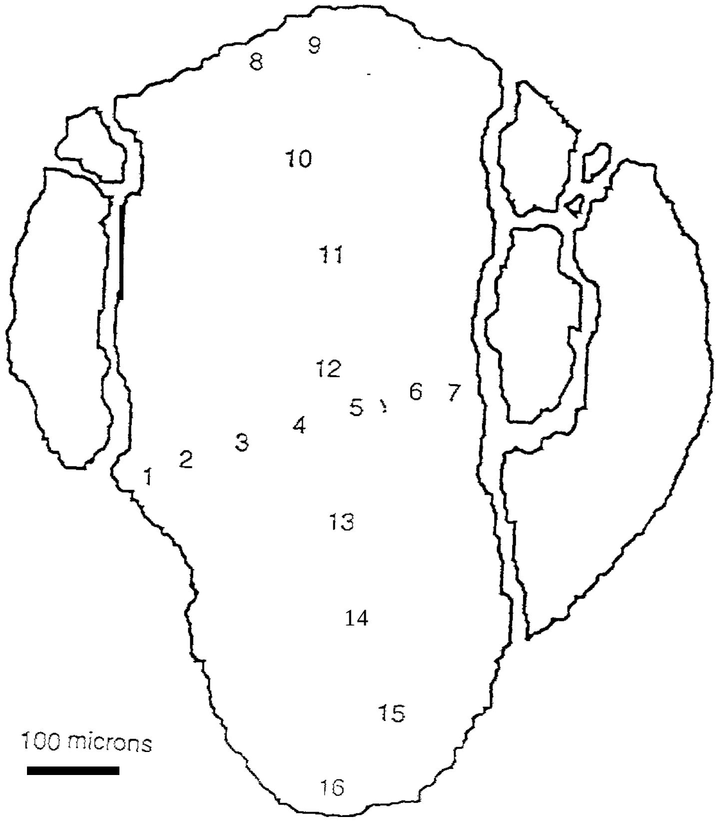


Fig. 19 Sketch of an olivine crystal from LVF C8 (29) selected for ion probe analysis. The numbers on the olivine refer to EPMA analysis points

Oxygen isotopes

Isotopic studies were carried out on three massifs in Madagascar: one barren at Bemongikely and two mineralized at Andohankiranomena and Lavatrafo to establish the origin of the mineralizing fluid, and the influence of hydrothermal metamorphism and low temperature weathering. Oxygen isotope data were obtained from barren and mineralized whole rocks and separated minerals.

Oxygen isotope data were obtained by conventional method, the laser fluorination method and by *in situ* analyses on chromiferous spinels (because of the close textural relationships between PGM and chromiferous spinels).

Mantle values were obtained for three pyroxenite whole rock samples and separated minerals from the "fertile" zone of the Andohankiranomena massif. The $\delta^{18}O$ varies from 5.5 to 6.0‰ for the whole rock samples, from 5.7 to 5.9‰ for the clinopyroxenes, and from 5.9 to 6.1‰ for the orthopyroxenes, slightly more enriched in ^{18}O compared to the clinopyroxenes. Higher values are obtained from the barren Bemongikely massif, from different rock types: pyroxenite, biotitite, granite, gabbro, dunite, peridotite. The $\delta^{18}O$ varies from 6.1 to 7.6‰ in the pyroxenites, and is 8.8‰ in the biotitite, 12.1‰ in the granite, 6.2‰ in the metagabbro, 6.9‰ in the dunite and 9.8‰ in the harzburgite. These values are all higher than normal values in fresh rock of mantle origin or differentiated from a primary basic magma.

The $\delta^{18}O$ in plagioclase and orthopyroxene analysed from a pyroxenite is respectively 7.5 and 6.5‰ and the fractionation between these two minerals corresponds to a temperature of around 700°C. The $\delta^{18}O$ in plagioclase and pyroxene analysed from the granite is respectively 8.4 and 6.9‰, with the fractionation between these two minerals corresponding to a temperature of 720°C.

The fact that the same temperature range is determined on two samples of different types indicates that it probably corresponds to the metamorphic temperature recorded by these rocks; the same temperature range of metamorphism was also determined from pyroxene, garnet and spinel by Johan (1992).

Moreover, the $\delta^{18}O$ of the granite whole rock is too high in relation to that of the minerals and probably reflects the presence of lower temperature alteration minerals.

The samples from the Bemongikely area show secondary alteration or re-equilibration phenomena which were not registered by the samples from the Andohankiranomena area. These appear to be relatively homogeneous since the sampling covered the whole of the Bermongikely area. Likewise, the range of data obtained from the Lavatrafo drill core is compatible with late requilibration and supergene alteration.

In-situ analyses of oxygen isotopes

At Lavatrafo, the magmatic signature of olivine was retained despite being in close proximity to extensive alteration ($\delta^{18}O_{SMOW}$ values of 5.1 ±1.8‰ using ion microprobe) (Fig. 19) (Lyon et al. 94; 95; Saxton et al., 1995). The olivine grains are large and relatively homogeneous at least along drill core LVF C8 ($Fo_{86\pm2}$), despite a slight Fe enrichment towards the rim, A magmatic signature was also obtained from spinel of the Albania massifs with the laser probe using the fluorination method ($4.3 < \delta^{18}O_{SMOW} < 4,8$).

Sulphur isotopes

Albania target

The low delta ($-4.4 < \delta S^{34}$ ‰ $< +2.9$ ‰) shown by sulphide-rich dunites at Bulqiza is compatible with an origin from a magmatic mineralizing fluid. An increase of in δS^{34} may be pointed out from residual pentlandite of the preserved early assemblage ($-3.3 < \delta S^{34} < -3.6$) to the oxidized pentlandite from late- stage assemblage ($-0.1 < \delta S^{34} < +2$).

Such variation of the δS^{34} could be assigned to serpentinization related to hydrothermal metamorphism or to autometasomatism during the settling of the Pd mineralization (T < 560°). Lower δS^{34} values ($-8.0 < \delta S^{34} < -7.5$ ‰) are also recorded for gold mineralization in arsenopyrite dyke occuring in the vicinity of the PGE deposit. This value excludes an origin from a hydrothermal process involving interaction between the oceanic crust and circulating sea water. One hypothesis for the emplacement of the gold rich dyke was a late-stage formation related to the emplacement of the PGE mineralization.

In situ analyses of sulphur isotopes from Lavatrafo and Bulqiza show a magmatic origin for the BMS associated with the PGE mineralization.

$^{187}Re/^{186}Os$ isotopes

Secondary and backscattered electron maps of large (300-400 microns across) Os-bearing alloys and sulfides from Albania were prepared to aid secondary ionization mass spectrometry (SIMS) studies using the ion probe (Fig. 19). The Albanian sample is a heavy mineral concentrate which is a composite of several PGE phases such as isoferroplatinum (Pt_3Fe), tulameenite (Pt_2FeCu), laurite (RuS_2), irarsite (IrAsS) and various Os-Ir alloys. The grains which were analysed were Os-Ir alloy (typically 20-50 wt% Os) and laurite which contains 3-16% Os by weight. With the exception of Grain 9 (which was composite of Os-Ir alloy, which contained an inclusion of laurite and was itself surrounded by irarsite and isoferroplatinum) the results represent the mean of several spots taken in a traverse across a single grain. In the case of Grain 9, the Os-Ir alloy and the laurite were analysed separately. The $^{187}Os/^{186}Os$ ratios obtained from these samples are shown in Table 5.

Table 5: Summary of in-situ Os isotopic data. Errors represent 2 standard deviations of the mean value for the grain, based on the analysis of 2-6 spots. “n. a.” indicates a present or future age calculated on the basis of the assumed mantle evolution trend (see task 4.5).

Sample	$^{187}Os/^{186}Os$	Model Age (Ma)
Grain 1 (alloy)	1.069 +/- 0.003	n.a.
Grain 4 (alloy)	1.091 +/- 0.006	n.a.
Grain 7 (alloy)	1.046 +/- 0.005	145 +/- 90
Grain 9 (alloy)	.048 +/- 0.005	120 +/- 90
Grain 9 (laurite)	.038 +/- 0.004	290 +/- 70
Grain 12 (alloy)	.061 +/- 0.006	n.a.
Grain 13 (alloy)	.039 +/- 0.005	270 +/- 90
Grain 14 (alloy)	.054 +/- 0.003	n.a.

The grains give a range of $^{187}Os/^{186}Os$ ratios between 1.038 and 1.091. This range is within that expected for the oceanic mantle in the early Mesozoic (the age range expected for the Albanian ophiolites). This range is comparable with the "within-province” ranges obtained by Hattori and Hart (1991) in their study of Os alloys from Alaskan complexes and placers at many worldwide localities. No evidence was found for the highly radiogenic ^{187}Os which has been reported from placer deposits in Sierra Leone (Hattori et al. 1991).

Model ages were calculated assuming the parameters adopted by Luck et al. (1988) and Hart and Kinloch (1989), namely a ^{187}Os/^{186}Os ratio of 1.054 in the present-day mantle, an initial ^{187}Os/^{186}Os ratio of 0.803 at 4.55 Ga and a Re decay constant = 1.52 x 1011 yr- 1. Half of the grains gave ^{187}Os/^{186}Os "ratios < 1.054 and produced model ages which range between 120-290 Ma which is consistent with the expected age range for the Albanian ophiolites.

However it is interesting that the laurite and the Os-Ir alloy analysed in Grain 9 show significantly different ratios and model ages. The laurite inclusion has a model age of 290 ± 70 Ma while the surrounding alloy has a significantly younger model age of 120 ± 90 Ma. This would indicate that either: the laurite is very much older than the alloy (i.e. the laurite is an inherited grain); or that they are really of similar ages but that the magma from which the alloy crystallized contained more radiogenic ^{187}Os than was present w-hen the laurite crystallized.

It is unclear whether there was a significant time difference (10's or 100's of Ma) between the growth of different alloy grains. For example, the absence of ^{187}Os/^{186}Os ratios significantly above the expected mantle range precludes the introduction of crustal (radiogenic) ^{187}Os in the near surface environment in recent times (cf. Bowles et al. 1986).

The grains with ^{187}Os/^{186}Os ratios> 1.054 may have formed at the same time as the low ^{1}870s/^{1}860s material and it seems most likely that the different ratios reflect (mantle-derived) heterogeneities in the melts from which they formed. There is no evidence for any large-scale input of highly radiogenic "crustal" 0s, as has been found in PGM from layered igneous complexes generated in continental settings, such as the Bushveld and Stillwater complexes, (Hart and Kinloch 1989; Martin 1989; McCandless et al. 1994).

Organic components

The Madagascar target

Gas chromatography - mass spectrometry (GC-MS) studies carried out using thermal decrepitation and pyrolysis (to 850°C) have indicated that H_2O and CO_2 are the most abundant volatile species in both the Lavatrafo (LVFC8) and Andohankiranomena (ADKC1) samples. There is no systematic difference between the volatile species in the mineralized and barren zones and the relative amounts of H_20 and/or CO_2 appear to be in accordance with the petrography of most of the samples, where hydrous and carbonate minerals form a significant portion of the rock.

Small amounts of CH_4 have been found in those Lavatrafo samples containing the greatest volumes of partially altered sulphides and it seems possible that the production of methane may be related to the secondary alteration of the sulphides. No methane was detected in samples from ADK Cl core, where the degree of alteration has been the more extreme and the original silicates (± sulphides) assemblage has been almost completely overprinted. This is very unfortunate as the compositions of the relic spinels at Andohankiranomena suggest that conditions in the magma may have been more reduced than at Lavatrafo.

Noble gas studies

Analyses for He and Ar isotopes have been performed on separated minerals taken from PGE-mineralized and barren samples from the Lavatrafo (LVF C8) and Andohankiranomena (ADK C1) cores (Fig. 20). The ratio of $^3He/^4He$ in the samples vs. the ratio in the atmosphere (R/R_a) is generally in the range 0.3-0.6. This is significant] higher than average crustal values (0.01-0.03) and strongly suggests that a mantle He component is present within the fluids trapped by cumulate olivine and pyroxene. There is no systematic difference in noble gas ratios between the mineralized and barren samples.

A high R/R_a value and a low $^{40}Ar/^{36}Ar$ value were found in the alterite sample which lie close to the ratios in air most probably indicate a strong element of air contamination in this sample.

Cl-rich mineralogy

All the studied targets were modified by hydrothermal metamorphism, especially the Madagascar intrusive. In Lavatrafo, the occurrence of hydrated phases is widespread even in the fresher rocks where phlogopite and amphibole (hornblende and tremolite) occur in interstitial areas.

Three distinct episodes involving different fluids have been distinguished from petrographic observation and Cl-distribution among the hydrated phases. The earliest (magmatic) fluids were active in the interstitial spaces of the dunites and pyroxenites, Cl-bearing, and led to the crystallization of phlogopite and hornblende (0. 16-0.38 wt%). Mica is generally more Cl-rich than hornblende (Fig, 21). Hornblende crystals are larger and more abundant that the mica and while many crystals have euhedral-subhedral forms. they are clearly moulded onto earlier BMS and spinel. Subhedral to anhedral phlogopite is also seen to be moulded against BMS and spinel but it encloses amphibole as well, suggesting that mica crystallization may have followed that of hornblende,

The intermediate (metamorphic ?) fluids which produced the tremolitic veins appear to have been Cl-poor. These veins cut across the early olivine and p yroxene. Chlorite, which locally replaces hornblende, is consistently chlorine-free. The latest low temperature fluids (<500°C) associated with serpentinization may also have contained chlorine.

Olivine in the mineralized and barren zones is strongly veined by serpentine. Analyses of the serpentine sometimes indicate the presence of small concentrations of chlorine (O. 12-0.18 wt%) but this is very erratic and may simply reflect the presence of sub-micron sized Cl-bearing phases (possibly halides) between the fibres of the serpentine.

There is stronger evidence for metamorphism in the Andohankiranomena intrusion. The original magmatic assemblage has been extensively altered to tremolitic and cummingtonitic amphibole, and chlorite. Cummingtonite and chlorite both contain significant concentrations of chlorine (O. 12-0.29 wt%) and where rare crystals of sylvite (KCl) have been observed, the surrounding chlorite is extremely enriched in Cl (up to 1.66 wt%). The tremolite is free of Cl. The Cl-rich mineralogy of the ADK C 1 core appears to have developed as a result of late stage (greenschist facies ?) metamorphism. This would support the absence of sulphides (other than those trapped and armoured by chromite grains) in the ADK C 1 core, as a secondary Cl-rich fluid would strong] y attack and replace any primary sulphide mineralogy. Fluids associated with this event apparently contained more Cl and less CO_2 than the low temperature fluids at Lavatrafo.

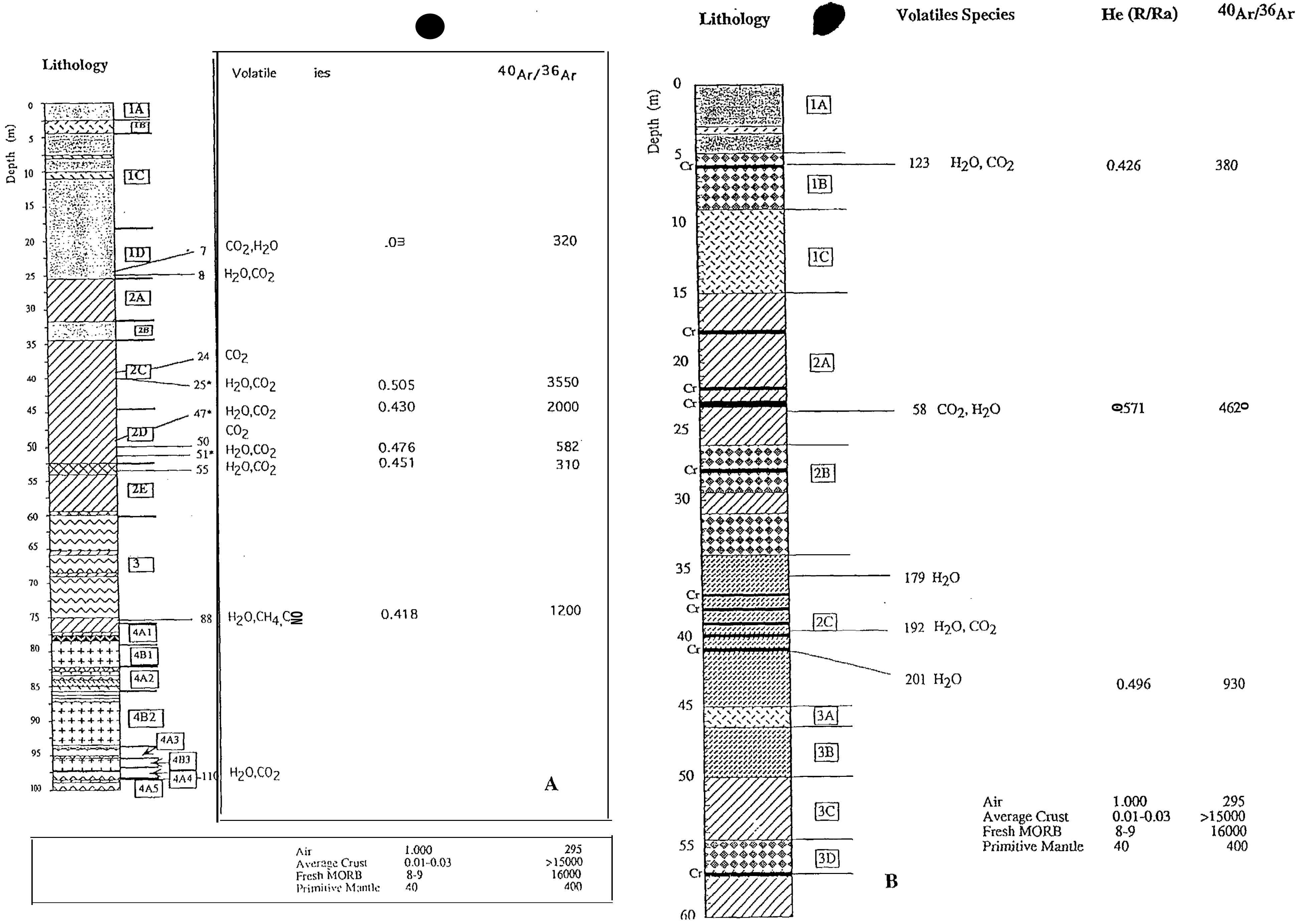


Fig. 20 A and **B**, C-H-O volatile and noble gases in Lavatrafo LVFC8 drill core and Andohankiranomena ADKC1 drill core, respectively.

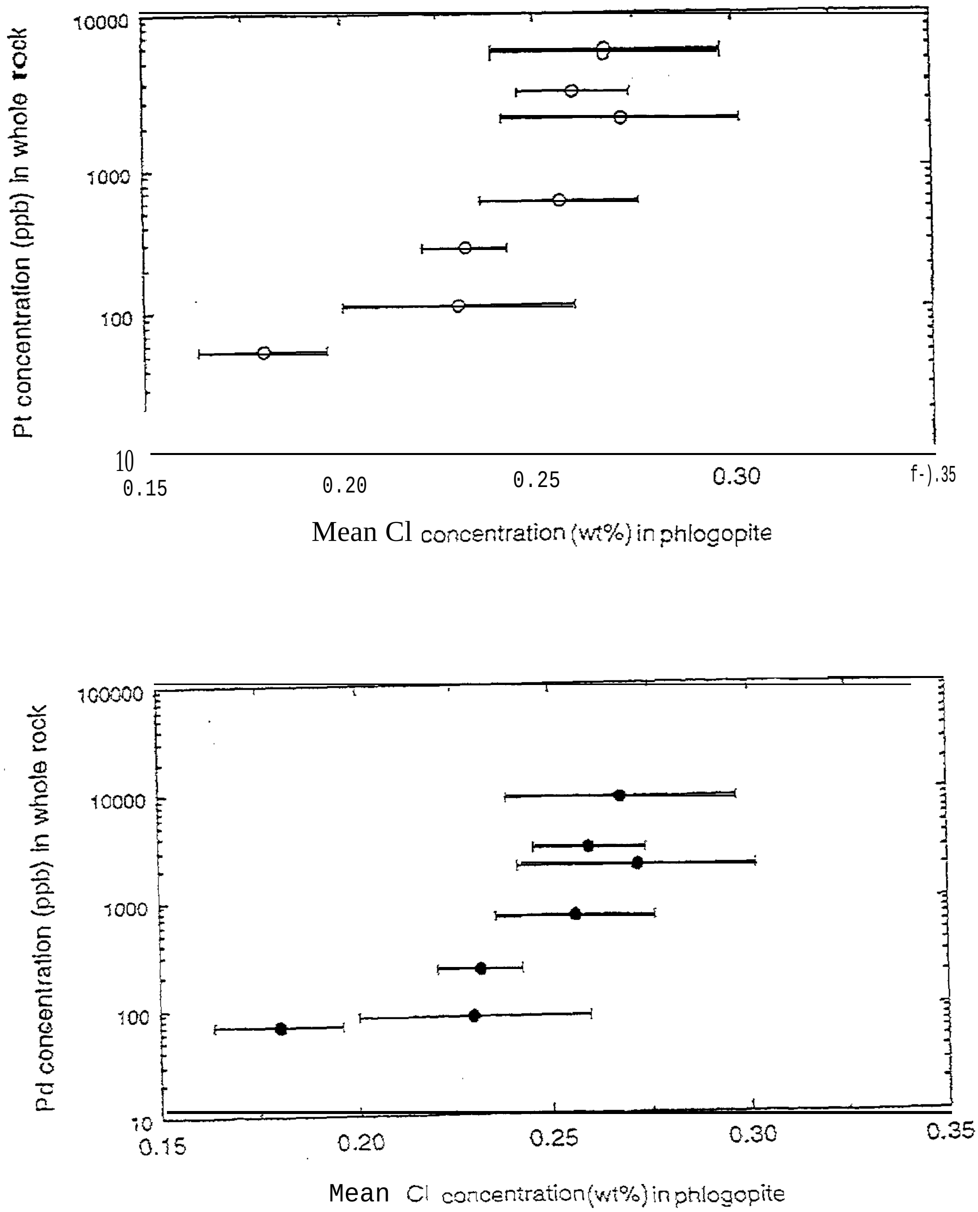


Fig. 21, Relationship between the Cl concentration of interstitial phlogopite and the Pt and p^{d} concentrations in the bulk rock. All samples from the LVF C8 core.

Model of emplacement for the Pt-rich chomitites

Pt-rich chromitites at Tropoja arid Andohankiranomena have the following common features:

(1) The presence of magmatic intrusions of reduced size, no more than 2 km long, The geological setting of lithological facies in dykes of variable thickness corresponds to an injection zone rather than to a well developed magma chamber." The zonal distribution of the different rock types is crude and highly disturbed by cross-cutting relationships. Dykes are predominant in the pyroxenitic zone, especially in the orthopyroxenite zone hosting the Pt-mineralization.

(2) The Pt-rich chromitites occur only in the upper chromite levels of basic-ultrabasic complexes. Lower chromite levels in ophiolites occur towards the base of the mantle transition zone (chromite pods) or in the lower part of the Upper Moho dunite zone. In the Andriamena area, the early chromitite occurs in pods and veins associated with olivine-bearing ultramafites later cut by orthopyroxenite dykes. The present-day mined massive chromite deposit of North Andriamena may correspond to this type of Pt-barren deposit.

(3) There is a close association in the field between dykes of pegmatitic pyroxenes and Pt-rich chromitites.

(4) Crystallization of chromite hosting the PGM mineralization occurred later than that of olivine and orthopyroxene, the latter one forming the matrix of the disseminated chromitites.

(5) Fe^{3+} content of chromiferous spinels hosting PGM is higher than that of spinels from the lower chromite levels.

The main differences between the two Pt-rich chromitite deposits bear on the geotectonic setting of the host basic-ultrabasic complexes and on the composition of parental magmas. The intrusion zone at Tropoja was developed in a faulted harzburgitic mantle during the opening of marginal basins. The intrusion zone at Andohankiranomena is located in a continental crust sheared during a pan-African rifting.

Pt-bearing PGM are mostly alloys at Tropoja and alloys and arsenides at Andriamena. However, the mineralogical assemblage could vary inside a deposit, For example, a Pt-rich chromite deposit at Tropoj a has arsenides besides the usual Pt-rich alloys, an assemblage which shows close similarities with the predominant PGM paragenesis observed in Andohankiranomena deposits.

It is proposed that chromitite were formed directly from an evolving silicate magma. Crystallization order of minerals [Ol - Opx - (Sp+Pt-alloys) - Cpx - Pl] deduced from the different rock assemblages below and above the mineralized zone, would rather indicate that Pt concentration occurred during magma fractionation, leading first to the formation of dunite and orthopyroxenite, and then to that of the mineralized chromitite.

The evolving magma is however enriched in hydrous components and other volatile species at the time of chromite and PGM deposition. Inclusions in chromite with coexiting PGM and hydrous phases as amphiboles and/or phlogopite mica. and giant orthopyroxenes, are evidence for the existence of magmatic fluids. Noble metals and related magmatophile elements were preferentially concentrated in such hydrous magmas located at the top of magma pockets or a magma column.

Hydrofracturing might have resulted in response to local fluid pressure increase and/or to lithostatic pressure decrease. This lead to the opening of magma conduits with variable orientation and the formation of magmatic breccias, locally cemented by chromite-rich pyroxenite. Turbulant magmatic conditions during dyke opening and magma migration contrast with quiescent period of sidewall pyroxene crystallization in dykes.

Based on Fe^{3+} variations in chromite grains hosting Pt-alloys, crystallization of PGM was enhanced by abrupt reduction of the oxygen fugacity. However, the lack of CH4 in the volatile phase and the absence of graphite, argues against processes involving rapidly fluctuating oxygen fugacity conditions and the high temperature precipitation of graphite as part of the development of the mineralization (Mathez et al., 1989).

The scarcity of sulphides is a good indication that the mineralizing system was sulphur-poor, considering experimental results obtained during this study. Nevertheless isoferroplatinum, which is predominant in tropoj a, could crystallize at variable S fugacity. Because of the presence of cooperite rimming isoferroplatinum in one rock, and of cooperite associated with $(Pt, Ir, Rh)_2S_3$ or $Cu(Pt,Rh)_2S_4$ minerals in some other rocks, high sulfur fugacities may have occurred during the crystallization of isoferroplatinum. Pt should have been extracted from a Cu-Fe bearing sulphide melt. The presence of disseminated sulphides above the Tropoja reef would indicate that such melt occurred.

Otherwise, isoferroplatinum could have crystallized from a S-poor melt at high temperatures (1100"C ≈ 900°C) from a S- rich mineralizing fluid. When the mineralizing system was enriched in As, Sb, Te, as in Madagascar, the crystallization of PGM carrying these elements was favoured. It is noticeable that a significant proportion of arsenides, antimonides and tellurides are preferentially found between the chromite grains rather than inside the chromite grains. This occurred in response to lower temperatures of formation or preferential entrapment of Pt-bearing mineralizing fluids between the chromite grains. Of course, late-stage remobilization of PGE by hydrothermal fluids may also explain such a PGM distribution (see later).

Zoned PGM and the presence of distinct mineral assemblage in rocks from Pt-deposit would indicate the existence of a fluid-driven multi-stage mineralizing process. The high temperature crystallization of isoferroplatinum is followed by the formation of Rh-rich alloys rimmed by Pt-Cu and Pd-Cu alloys crystallized at lower temperature. These different mineralizing stages are observed in distinct rocks, in agreement with fractionation of the PGE-mineralizing system.

Model of emplacement for Pt-rich silicate rocks poor in base metal sulphides

Common features between the Bulqiza and the Lavatrafo mineralization are based on the existence of a barren dunitic matrix which contrasts with the mineralized interstices showing the PGM paragenesis. There, PGM are associated with a variable proportion of BMS, locally enriched in PGE, chromiferous spinels, clinopyroxene, amphibole, orthopyroxene and phlogopite, the latter two phases being restricted to Lavatrafo intrusive. Mineral composition can vary strongly with stratigraphy as for chromiferous spinels.

Discrepancies between the two deposits bear on:

(1) the geotectonic setting of the intrusive and correspondingly on the nature of parental magmas;

(2) the genesis of the dunitic matrix, which may be a crystal mush emplaced in dyke at Lavatrafo, or a strongly depleted mantle left after partial melting or a resulting product of mantle metasomatism of harzburgite at Bulqiza, possibly during chromite deposit formation (Arai and Yurimoto, 1994);

(3) the shape of the dunitic bodies. Narrow dyke-like bodies belonging to a feeder zone exist at Lavatrafo. A massive, homogeneous body of variable thickness (up to 1 km) and extent occurs between the mantle harzburgite and the pyroxenitic or gabbroic sequence at Bulqiza;

(4) the shape and extent of the mineralized zones. The shape of the wide mineralized bodies at Lavatrafo is moulded on the dyke margins. Disseminated sulphides form a discontinuous reef in the upper part of the supra-Moho dunite zone at Bulqiza;
(5) the paragenetic PGE-rich assemblage. Several mineral species of medium-grain size. but dominated by arsenides, exist at Lavatrafo. Only few PGM of small size associated with BMS have been recognized at Bulqiza.
(6} the association of BMS (pyrrotite, chalcopyrite and pentlandite at Lavatrafo in both mineralized and barren dunites, whereas pentlandite predominates at Bulqiza).

A common model of emplacement of Pt-mineralization may be proposed for the two mineralized sites despite their differences. The mineralizing system is thought to be related to a Pt-rich fluid derived from the interstitial melt migrating through an unconsolidated dunitic matrix. This fluid carried noble metals, transition elements. alkaline and talc-alkaline elements, incompatible elements and volatile species. These elements might have entered the accessory minerals responsible for the diversity of the assemblages observed in interstitial areas. The composition of some minerals, e.g. spinels, may vary strongly with stratigraphy according to the chemical evolution of the migrating mineralizing fluid. Fractionation of mineralizing fluids was enhanced by low fluid/rock ratio, a fact deduced from the few reactions observed between the interstitial material and the host dunite, and from the low proportion of interstices between olivine.

The chemical evolution of the mineralizing system was possible because voids between olivine were kept open during cooling as suggested by the observed textures. In ophiolitic dunite, coarse-grained textures were achieved only under low deviatoric stresses. In the Lavatrafo intrusions, mineralizing fluids were collected in tension gashes related to strike-slip tectonics.

In both Bulqiza and Lavatrafo sites, cooling time was long enough to make possible fluid percolation through dunite and subsequent Pt-deposition in pores. The maximum time span for ophiolitic accretion is about 40 My (Lias-Upper Jurassic). During the oceanization processes, dunites were kept warm because of the presence of a harburgitic mantle below which was affected by partial fusion processes shlighly before or even during the formation of dunites. An early formed cumulates above dunites prevented also from a too rapid cooling.

The data in West Andriamena indicate that the Pt mineralized bodies were emplaced during a restricted time interval (< ≈ 20 Ma) between the emplacement of the ultramafic intrusions (787+16 Ma) and that of the granite dykes (762+17 Ma) which interrupted the Pt-Pd distribution patterns. Late stage Pt- and Pd- barren fine-grained pyroxenites, usually at the margin of the intrusions in Andohankiranomena, and gabbroic rocks, cutting' the mineralized dunites at Lavatrafo, were probably emplaced after deposition of the Pt-mineralization for similar reasons as for granite. It seems unlikely that a difference in porosity between dunite and late fine-grained pyroxenitic and gabbroic rocks would explain the Pt and Pd distribution. If pyroxenites and gabbros were emplaced before the Pt-rnineralization, they would have been mineralized with duni te. Furthermore, the dyke margin would have been a preferential site for entrapment of the mineralizing fluid. However, no noticeable Pt enrichment is observed close to the dyke margins.

In Lavatrafo, the initial temperature difference between the magma and granulite facies wall rocks is low (<400°C). There is some evidence for interactions between the mantle derived melts and the host granulitic crust: a second subvertical foliation marked by recrystallized biotite is superimposed on the early slightly inclined foliation. in response to shearing at the margins of the intrusions. A second generation of zircon recrystallized in the host granulitic crust close to the ultramafic intrusive.

According to a thermal diffusion model, a dyke thickness of 200 m is enough for a basic magma to remain above its solidus for a long time. Slow cooling of basic melts leads to the crystallisation of dunite and related ultramafites, and to the migration of residual melts during convective fractionation. Concentration and chemical evolution of mineralizing fluids towards tension gashes with cooling resulted in preferential enrichment of PGE and decrease of the Pt/Pd ratio in the core of the intrusion.

Discussion

High temperature hydrothermal activity and late-stage magmatic fluids

Evidence for PGE secondary mobilization related to high or low temperature hydrothermal activity during the cooling of the intrusions is obvious in all the studied targets. This is expressed by a new mineralogical assemblage carrying the PGE, with remnants of the early PGM still locally preserved, by variation of the PGE contents and Pt/Pd ratios and by change of the sulphur and oxygen isotopic ratios, and by the predominance of H_2O and CO_2 amongst the volatile species.

The original PGM-bearing assemblage of the Pt-rich chromitites escaped significant secondary alteration because most of PGM are included in chromite. Part of the early mineralizing fluids were trapped in inclusions where daughter minerals crystallized in a closed system with only restricted reactions with the host chromite. The magmatic or hydrothermal origin of the interstitial PGM is much more debatable, because residual magmatic fluids and external hydrothermal fluids might have migrated between the early crystallizing minerals at decreasing temperatures. Similar questions on the PGE origin may be asked for Pt-mineralization in silicate rocks due to the existence of interstitial material between early olivine.

In West Andriamena, the extent of alteration and the nature of fluids evolved from place to place, as recorded by the Cl contents of the successive amphiboles and micas. relate to the three different hydrothermal stages. No doubt local remobilization of noble metals occurred, especially during redox processes related either to serpentinization or supergene alteration. PGE mobility may be enhanced by Cl ions in this system (Saini-Eidukat et Kucha, 1991), This was followed by precipitation of PGE and gold, not far from the original site of deposition, to preserve the original distribution of noble metals. A magmatic origin for sulphides and late stage remobilization of base metals and noble metals was proposed for some PGE deposits (Good and Crocket, 1994) whereas for other an hydrothermal origin is retained for the PGE mineralization (Watkinson and Ohnenstetter, 1992). Quartz-rich veins and volcano-sulphide deposits may host hydrothermal PGM (Crocket, 1990; MacDonald et al., 1995).

In Lavatrafo, mass-balance calculations applied to the size of the mineralized bodies with respect to the host rocks, and their respective Pt contents, indicates that the mineralizing fluids do not derive only from an in-situ magmatic process, but also have an external origin, being issued from deeper and probably wider magma chambers. This hypothesis is compatible with the sulphur isotope data and with the presence of numerous ultramafic intrusions emplaced in the crust in the West Andriamena area. Magmatic fluids derived from crystallization of basic magmas at depth were later pumped and collected by Lavatrafo dyke-like intrusions.

The process of volatile transport is currently retained for the genesis of mineralization associated with granitic intrusions (Tobish and Cruden, 1995). In contrast to such deposits located around the granitic apex or disposed along radial and concentric veins, PGE deposits at Lavatrafo and Bulqiza occur inside the intrusive. The shape of mineralized bodies at Lavatrafo and the setting of the mineralized reef at Bulqiza are controlled by igneous planes. In both cases, the mineralized assemblage is located in interstitial areas between early olivine, opened during magmatic processes.

In West Andriamena, amphibolite to greenschist facies metamorphic assemblages are widespread but more particularly developed along shear zones cutting both the intrusives and the continental shield. These features recall the channeling of gold-rich fluids along deep shear zones in gold mineralized continental areas (Bonnemaison, 1987: Bonnemaison and Marcoux, 1990; Cameron, 1993). In Andriamena, no noticeable Pt- and Pal-enrichment occurs along subvertical shear faults. However, the influence of shearing on the distribution of the Pt-mineralization is evident since the oblique opening of continental crust, which controlled the shape and extent of the intrusions and those of related mineralized bodies.

There is some similarity between the mineralogical and chemical zoning of' hydrothermal deposits and that recorded in the studied targets. The large chemical evolution of the spinel compositions is a striking feature, more especially for Pt-mineralization of silicate rocks. At Bulqiza, the abrupt variation of the spine] composition along a 200 m section in dunites, contrasts with the smooth variation of chromiferous spinel compositions in lower mantle rocks and related massive chromite deposits, and in upper pyroxenitic or gabbroic rocks. Furthermore, refractory spinels characterizing Pt-enriched chromite or dunite are also found in gold-bearing arsenopyrite veins close to the Moho, in association with ilmenite and rutile, for which a hydrothermal origin is proposed.

In the other studied deposits, chromiferous spinels show a Fe^{3+} enrichment coupled with distinct Al-Cr variation. In West Andriamena, two trends of spinel composition may be defined, one of them showing an enrichment in the ferrichromite molecule, is related to a serpentinisation process. The other with a coupled Cr and Fe^{3+} enrichment is due to an earlier process which may be related to the magmatic evolution of the complexes. The fact that Lavatrafo chrome spinels are richer in Fe^{3+} and Cr compared to the Andohankiranomena spinels is in agreement with the more evolved character of the Lavatrafo-type intrusions.

At a smaller scale, distinct core-rim variation of spinels according to the nature of the adjacent minerals is not compatible with a serpentinization process but with late-stage magmatism or subsolidus reactions.

Pt-mineralization and magmatic processes

Although no single dataset provides unequivocal evidence, indications of the involvement of a magmatic fluid in ore genesis comprise:
(1) location of the PGE deposits inside the intrusive rocks, especially along magmatic lithological planes such as layering planes or dyke margins, or inside voids as the interstitial areas between early crystallized minerals;
(2) the cryptic evolution of the associated minerals with stratigraphy or from the margin to the core of dunitic dykes;
(3) the high temperature of the Pt-rich chromitite formation and the lower temperatures for Pt-mineralization related to the interstitial melt evolution;
(4) the magmatic sulphur and oxygen isotope signature of the Bulqiza and Lavatrafo deposits;
(5) the presence of a He mantle component in Andriamana intrusive.

There is no evidence for the existence of magma mixing often considered as an external mechanism involved in the formation of Pt-Pd concentration either related to chromite or sulphide deposits (Lambert et al. 1994). Such a model involves the injection of a new magma pulse enriched in PGE in the magma chamber. followed by mixing with the resident magma. The PGE reefs are formed in response to this process leading to major physico-chemical changes at the bottom of the magma chamber.

The magma mixing model is difficult to apply to Pt-deposits hosted by dunites because of the setting of the Pt-mineralization. This Pt-mineralization seems to be formed during migration of the interstitial melt through the dunitic mush and not at the interface between two magmas. Of course, a double convective process may be proposed to trigger magma migration.

The magma mixing model may be also neglected for Pt-rich chromitites because the setting of the narrow chromite-bearing dykes is difficult to reconcile with long-time convection and mixing of two magmas, one deriving from the stagnant magma and the other from ascending magma pulses coming from the mantle. Subhorizontal shear zones and movements deduced along faulted dyke planes indicate an upwards migration of the melt in dykes relayed by sheared horizontal veins.

Moreover, normal zoning of minerals in the studied targets is against magma mixing. The time of PGE precipitation can be defined in the course of magma fractionation related to chromite crystallization, as shown by the Tropoja and Andohankiranomena deposits, or during late-magmatic processes, durirng the migration of residual magmatic fluids between early mineral grains.

The fact that the chemical variation of chrome spinel in the Bulqiza dunites encompasses that recorded in lower and upper ophiolitic rocks raises some questions on their respective magmatic linkage. If mineralized dunite is genetically related to gabbro lying above, because of the presence of refractory spinels in both cases. the interstitial melt migrating through the Supra-Moho dunites might have fed the crustal chamber giving later rocks of the gabbroic sequence. All of these rocks have plagioclase as an early crystalline mineral, before pyroxenes. The absence of plagioclase in the mineralized dunite, and conversely the presence of clinopyroxene in interstital areas argue against a direct genetic link between the mineralized rock and the gabbroic sequence.

The association of olivine, clinopyroxene and chromiferous spinel, usually observed in interstitial areas of dunites, characterizes rock assemblage of the ultramafic sequence. Based on this common mineralogical assemblage, the origin of the Pt-mineralized Cpx- and BMS- bearing dunites may be related to that of the ultramafic sequence, possibly emplaced later than the gabbroic sequence.

The evolution of chromite composition in the mineralized dunite with stratigraphy is similar to that observed in mantle chromitites from early deep Pt-barren (1-rich deposits to more superficial late Al-rich deposits often enriched in Pt. Hence, Pt-mineralization in mantle and in supra-moho dunites may result from the same mineralizing process which affected distinct hosts: mantle harzburgite and Supra-Moho dunites.

In the Bregu i Bibës area, evidence for emplacement of different crustal sequences with contrasting characters is lacking, in opposite to Bulqiza ophiolites. Because of the early crystallization of orthopyroxene with respect to clinopyroxene, parental magmas in the Bregu i Bibës injection zone were more Si-rich than those of the Bulqiza crustal sequences, This is also compatible with higher Cr content of chromitite deposits in the Bregu i bibës area.

Parental magmas in the Andriamena areas are continental tholeites being more or less Si-saturated and enriched in alcaline and incompatible elements. Magmas at lavatrafo are iron-richer than the one parental to Andohankiranomena intrusions.

The Tropoja injection zone was created in a marginal basin} immature island arc environmnent inside an harzburgitic mantle. The West Andriamena intrusions are related to a pan-african rifting process leading to the formation of multiple magma pockets undertapping the continental crust. In all of these cases, contamination of the mantle source rocks by fluids before or during partial melting modified the resulting magmas. In the Albanian ophiolites, contamination in the upper mantle wedge due to the subducting plate, changed substantiality the distribution of elements and the fluid content of the derived parental magmas, compared to dry Mid-Oceanic ridge melts. In Madagascar, a strong crustal metasomatism modified the trace element distribution and especially the radiogenic isotope ratios. Such fluid contamination may have enhanced the concentration and deposition of base metals and noble metals during magma fractionation at lower levels in crustal magma chambers.

Furthermore, it maybe emphasized that the contamined melts generated either in a continent or in an island-arc type environment have a higher metallogenic potential that the "dry" uncontaminated mid-oceanic type melts.

Cr, Ni, PGE and Au mineralization in basic-ultrabasic complexes

Present-day mined platiniferous deposits are usually associated with base metal sulphides (BMS). PGE could represent the main product (Merensky Reef, Bushveld, J.M. Reef, Stillwater) or a by-product of the mine exploited for Ni and/or Cu (Sudbury). Indeed, the generally accepted model for magmatic concentrations is based on the collection of PGE by an immiscible BMS melt separated from the silicate magma. The origin of sulfur may be magmatic or crustal according to the extent of contamination processes. According to this hypothesis, no genetic relationships are expected between the different mineralizations which occur in basic-ultrabasic complexes, notably because the BMS melt collection is incompatible with PGE concentration in chromitite or in silicate rocks devoid of significant BMS.

The project realized during three years permits to study Pt-deposits devoid of significant BMS from four mineralized intrusions, and to develop two models applied to Pt-rich chromitite and to Pt-rich silicate rocks, respectively. These models may be integrated in a global metallogenic process developed from the different types of mineralization observed in a basic-ultrabasic complex, during silicate magma fractionation in magma chambers. Three metallogenic stages may be defined from a fluid-driven metallogenic process. The two later stages correspond to the emplacement models proposed for Pt-mineralization devoid in BMS.

First stage:

Crystallisation of deep Pt-barren massive chromite, having usually a high XCr [XCr = Cr/(Cr+Al)]. PGE distribution pattern is negative. This deposit corresponds to deep mantle chromitite of the transition zone in the Bulqiza and Tropoja ophiolites. Because of the selective sampling of the coarser chromite deposits in ophiolites, it was supposed for a long time that ophiolites were probably barren of Pt deposits. In Andohankiranomena type intrusive, the early large chromite pods are often Pt-depleted.

Second stage:

Crystallization of late Pt-enriched massive to disseminated chromitites, usually having a lower XCr ratio. This type of deposit was studied during the E.U project at Andohankiranomena and Tropoja. They are strati graphically above the Pt-barren chromitite or occurr in late dykes cutting rocks hosting the Pt-barren chromite deposits. Both settings exist in ophiolites.

Pt-rich chromitites may be variably enriched in Ru, Ir and 0s. In fact, there is a gradation between first stage Pt-barren chromitites and second stage Pt-enriched chrornitites marked by variable (Pt+Pd+Rh)/(Ru+Ir+ Os) ratios, and variable contents of Pt and Ir and Rh. There is a correlation between the evolution of PGE ratios and PGE contents, and the chemical evolution of the spinel composition.

Magmatic fluid activity is more evident during the second stage than in the first, due to the presence of hydrous minerals in inclusions, pegmatitic pyroxenites and hydrofracturing processes. Pt-rich chrornitite may result from direct crystal lization of

PGM from an H_2O-rich silicate melt, entraped in chromite at high temperatures. The Pt/Pd ratio is usually above 1 because of the predominance of alloys, especially isoferroplatinum. This indicates that Pt was concentrated in alloys, whereas Pd, and to a lesser extent Rh, were able to move on, together with the mineralizing fluid either S-rich or As-rich. In the Pt-rich chromitites, Pt/Pd decreases towards 1 when the nature of PGM is more variable with the presence of arsenides, antimonides, tellurides. In this case. PGM are not systematically included in chromite grains.

Third stage:

Formation of Pt-rich silicate rocks with no to accessory BMS. During the development of the EU project, Pd deposits devoid of BMS were studied in Lavatrafo intrusive and Pt-deposit with accessory BMS were studied at Bulqiza. As for BMS. chromite is never totally absent in rocks related to the third stage of mineralization. A common mineralizing model may be applied to both targets whatever the proportion of BMS. It involves the existence of mineralizing fluids derived from an intercumulus silicate magma which circulated through unconsolidated rocks during cooling.

In a sulphur-rich system, base metal sulphides and associated Pt and Pal-bearing sulphides will crystallize preferentially. The Pt/Pd ratio is usually below 1 because of the predominance of Pal-bearing sulphides. In a sulphur-poor system, BMS are rare. PGE are carried by their own mineral species: arsenides, antimonides and tellurides. The Pt/Pd ratio is closer to 1 in arsenide-rich deposits because of the stability of sperrylite for a wide range of temperatures.

In contrast to chromite deposits, Pt-deposits of the last mineralizing stage are gold-enriched, A decoupling is observed between Pt-Pd anomalies and the Au anomaly. The distance between anomalies varies for each deposit. They are not always associated wit h a BMS-rich horizon, the Au-enriched zone being located usually above the B MS horizon.

All the Pt and Pd deposits have an evolved character based on the (Pt+Pd)/(Os+Ir+Ru) ratio which is usually higher than 1. The location of the PGE reef near the top of the ultramafic zone in most of the large layered complexes, or within late-stage chromitites, as in ophiolites, is compatible with noticeable PGE fractionation before the formation of the deposits (Tredoux et al., 1995).

The evolution of PGE fractionation with stratigraphy can be related to the chemical composition of the associated minerals. This is more specifically shown by the correlation between the (Pt+Pd) content of the bulk rock and the Al_2O_3 content of chromium spinels in podiform chromitites, or by the Pt/Pd variation of bulk rocks with Al and Fe^{3+} contents of the chromium spinel. Evolved silicate-melt inclusions in isoferroplatinum minerals also indicate significant fractionation of the mineralizing system.

The fractionation of a highly mobile mineralizing fluid, generated from an intercumulus magma, would explain the gap between the sulphides and the PGM crystallization, Crystallization of PGM is inconsistent with simple exsolution from magmatic sulphides. Low S content in the mineralizing system under relative high fO_2 would favour the formation of arsenide deposits. Under more reducing conditions, the siderophile tendency, especially of Pt, would promote the crystallization of alloys. High S content would favour the chalcophile tendency of PGE and their close association with BMS deposits, In all the cases, fractionation of the mineralizing fluids results in zoned mineral assemblages, as noticed also for the Strathcona deposit (Li and Naldrett, 1993).

There are similarities between late magmatic Pt- and Pt- rich concentrations and high to low temperature hydrothermal deposits. Tarkian and Koopman (1995) have shown that porphyry copper-gold deposits may be enriched in Pd and Cu, and to a lesser extent in Pt. A chemical zoning may be observed, in response to successive crystallization of minerals carrying base metals and noble metals at a different place and time. Compositions of accessory minerals may show a strong chemical variation in relation to the evolution of the mineralizing fluids.

Application of a three stage metallogenic process to the Bushveld complex

This three stage metallogenic process relating chromite, sulphide and noble metal mineralization may be tentatively applied to the Bushveld complex. Cr, base metal and PGE mineralizations occur in the Critical zone located above the Lower Ultramafic zone and below the Main zone composed of mafic rocks, mostly gabbros and anorthosites. The occurrence of lower chromite levels at the base of the Critical zone, with high XCr and no Pt-enrichment, correspond to the first stage of the mineralizing process.

Characteristic features of the Pt-enriched upper chromite levels, comprising the UG2 reef, maybe compared with metallogenic products of the second metallogenic stage. From the Lower chromite level to the upper chromite level, XCr of chromite decreases and the Pt content increases together with the (Pt+Pd+Rh) / (Ru+Ir+Os) ratio (Scoon and Teigler, 1994). High Rh content in Pt-rich chromite was an important factor in deciding to mine the UG2 reef.

The third metallogenic stage may correspond to processes leading to the Merensky reef mineralization. The Merensky reef is located only a short distance above the UG2 (few meters to 100 m). The nature and proportion of the early cumulus minerals in the Merensky reef are highly variable, the host silicate rock being olivine-, pyroxene-, or even plagioclase-rich. The proportion of disseminated and interstitial BMS is small (1.5 wt. %) compared to other sulphide magmatic deposit. BMS may disappear in the Rustenburg facies showing silicate rocks bordered by two chromite seams. All of these facts are compatible with an origin of the Pt mineralization related to the evolution of the intercumulus material, rather than with the early crystallizing minerals.

VII. CONCLUSIONS

Four platiniferous deposits were studied during the EU project so as to propose a new model for the genesis of Pt- and Rh-rich platinum - group element (PGE) concentrations in the absence of significant base metal sulphide (BMS) mineralization. Based on mineralogical and metrological evidence, two types of deposits were recognized. those associated with chromitites (Tropoj a, Albania and Andohankiranomena, Madagascar targets) and those occurring in silicate rocks, mostly dunites, devoid of significant BMS and chromite concentration (Bulqiza, Albania and Lavatrafo, Madagascar targets).

The genesis of both types of PGE- mineralization is related to a fluid-driven multi-stage mineralizing process involving a fractionating silicate magma in a magma chamber. The mineralizing process leads first to crystallisation of Pt-barren massive chromitite. followed by crystallization of Pt-enriched chromitite, and finally by deposition of Pt-rich silicate rocks. In the final case, Pt concentrations derive from mineralizing fluids issuing from an ascending intercumulus silicate melt.

Gold mineralization was discovered during the EU project in Pt- and Pd- rich silicate rocks. Gold and (Pt+Pd) anomalies are often decoupled because noble metals are fractionated in the mineralizing system. The range of temperatures and sulphur fugacities for alloy-type mineralization associated with chromitites were determined from experimental studies during the project. From the early emplacement of chromitites to the late stage Pt and Pd deposition in silicate rocks, the temperature of formation decreases from magmatic (≈ 1100”C) to hydrothermal and even lower than the stability temperature of pentlandite (< 560°C). The origin of the mineralizing system was determined from a multidisciplinary approach, integrating the mineralogical composition of the PGE reef, the distribution of PGE, incompatible and volatile elements, and data from stable and radiogenic isotopes, All of the data are compatible with a magmatic origin of mineralizing fluids. However, no geochemical halo was recognized around the mineralized bodies in Madagascar.

The metallogenic process proposed for basic-ultrabasic complexes devoid of significant 13 MS, studied during the EU project, may be applied to those complexes with PGE mineralized reefs, associated either with chromitite or with disseminated BMS. More especially, the mineralizing system may be applied to the Bushveld complex, which controls about 60% of the total world production of PGE. The origin of these deposits is distinct from those showing sulphides at the margin of the intrusions, as in the Duluth complex, the Muskox intrusion, the Insizwa complex and the Cape Smith belt (Barnes and Francis, 1995). In such cases, the role of crustal mineralizing fluids is more significant.

Prospecting guides for Pt- and Pd- deposits are deduced from the fluid-driven multi-stage mineralizing system developed to model the origin of mineralization (Cr, Ni-Cu, EGP and Au) hosted by basic-ultrabasic complexes. High metallogenic potential of a basic-ultrabasic complex is suggested by the presence of chromite deposits. Pt- and Pd-e mineralization has to be sought for in silicate rocks above the upper chromite reef. The presence of BMS in such rocks is dependent on the S content of the whole system.

From the present study, it may be emphasised that the scarcity of base metal sulphides (BMS) in a basic-ultrabasic complex does not imply that no Pt-Pd mineralization exists.

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