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ABSTRACTS

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PREFACE

The 5th International Platinum symposium will be held in Otaniemi, Finland, on August 1–3, 1989. The symposium is organized by IAGOD Commission on Ore Deposits in Mafic and Ultramafic Rocks and is sponsored by the Society of Economic Geologists, the Geological Survey of Finland and the Geological Society of Finland.

Previous Platinum Symposia focused on ore deposits, geology, mineralogy and geochemistry of the platinum-group elements (PGE). These subjects are still topical in 1989.

Owing to centralized production and growth in demand for PGE in modern industrial applications, PGE have become strategic precious metals. Exploration for PGE has therefore increased in all parts of the world, and knowledge of their geology and geochemistry has grown along with the accumulation of accurate analytical data. More and more interest is being shown not only in deposits associated with fractionation of mafic magma but also in those in other environments such as ocean floor and other sedimentary strata. Hydrothermal and metamorphic mobility and accumulation of PGE are a subject of keen study and lively debate and new experimental data have now been reported on the hydrothermal origin of PGE deposits.

Almost 90 papers were submitted to the 5th Platinum Symposium. This is far greater number than it would be possible to present orally during the Symposium. The organizers had a difficult task compiling the programme so that our large audience would be equally interested in the oral presentations and the poster display. The Geological Society of Finland kindly offered space in the Bulletin of the Society for publication and distribution of the latest data on PGE. Topical classification of the abstracts was made by the editor. I thank the personnel of the Department of Geology, University of Turku and Mrs. Soile Glumoff for preparing of the manuscripts ready for printing.

Turku, June 1989
Heikki Papunen

1. PGE IN LAYERED INTRUSIONS

1.1

VERTICAL AND LATERAL VARIATIONS IN THE PETROLOGY, STRUCTURE AND MINERAL CHEMISTRY OF CYCLIC UNIT 1 OF THE DARWENDALE SUBCHAMBER OF THE GREAT DYKE, AND THEIR BEARING ON PGE AND BASE METAL MINERALIZATION

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The Great Dyke of Zimbabwe is a highly elongate intrusion with wall/floor rocks dipping at shallow angles towards a central dyke-like feeder and comprises two main magma chambers (North and South Chambers). Each of the magma chambers is divided into a number of subchambers on the basis of structural and lithological breaks along the length of the Dyke. Those in the North Chamber are (from north to south) the Musengezi, Darwendale and Sebakwe Subchambers. This study concerns the largest subchamber (Darwendale) which is 175 km long and up to 10 km wide. The layered succession of the subchamber consists of a lower Ultramafic Sequens (2000 m thick) overlain by 1000 m of the Mafic Sequence. The Ultramafic Sequence is broadly divided into the lower Dunite Succession and the upper Bronzitite Succession, the latter comprising cyclic units with a basal chromitite, overlain by dunite or harzburgite and passing upwards into bronzitite. Cyclic Unit 1 occurs at the top of the Ultramafic Sequence and represents the critical transition from olivine and bronzite cumulates through websterite into the overlying mafic rocks.

Cyclic Unit 1 is divided vertically into six subunits (1a-1f) on the basis of lithologies and mineral compositions. In the axis of subchamber the base of Subunit 1a is marked by a narrow (<3 m thick) olivine bronzitite layer, and although this layer dies out towards the margins, the boundary between subunits remains identifiable by marked changes in grain-size and mineral compositions. The upper part of Subunit 1a is a websterite which imediately underlies the gabbronorites of the Mafic Sequence. PGE enriched sulfide mineralization is contained in Subunits 1a and 1b. In Subunit 1b the mineralization occurs as a broad (10-20 m wide) disseminated zone with less than 2% sulfide. This contrasts with the sulfide mineralization of Subunit 1a, located at or just below the base of the websterite layer, which is much narrower (1-2 m wide) but contains up to 10% sulfide and is of potential economis importance. Cyclic Unit 1 as a whole becomes much thinner towards the margin and more orthocumulate in character. This lateral variation has a marked influence on the mineralization. Towards the margins of the subchamber the uppermost sulfide zone becomes highly compressed and strongly enriched (in the whole rock) in PGE and base metals over a shorter vertical iterval compared to the axis. Conversely there is a decrease in concentration of PGE's and base metals in sulfide in the whole rock towards the margin. The lateral variations in mineralization and layering characteristics are asymmetric across the geometric axis of the Darwendale Subchamber and, compared to the axis, the eastern side shows less extreme differences than the west side.

Cumulus bronzite of Cyclic Unit 1 shows a relatively small but progressive decrease in En content upwards in the succession as a result of *in situ* crystallization and fractionation. Reversals in mineral compositions are attributed either to minor influxes of primary magma or overturns within the chamber. The olivine bronzitite at the base of Subunit 1a resulted from a larger influx of magma temporarily driving the system back into the olivine phase field. Pyroxene compositions in the upper bronzitites of Subunit 1a adopt a trend of markedly increasing iron content towards the base of the Mafic Sequence. The rapid transition from bronzite through augite cumulates to the first appearance of plagioclase on the liquidus, as well as the iron enrichment trend, are iterpreted to result from mixing of a relatively primitive magma at the base of the chamber with more evolved liquid derived from the roof. Erosional structures at the top of the websterite layer may be related to this mixing event which also induced precipitation of sulfides.

These complex lateral relations reflect the strongly varying thermal conditions on the magma chamber due to its flared or trumpet shaped structure in transverse section. In this part of the succession effective heat loss would have taken place from the wall/floor as well as from the roof. Relatively small irregularities in the floor of the chamber may have had a marked local effect on the styles of crystallization, mineralization and layering characteristics.

1.2

DISTRIBUTION AND CONTROLS OF PLATINUM GROUP ELEMENT MINERALIZATION IN CYCLIC UNIT 1 OF THE GREAT DYKE, ZIMBABWE

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The uppermost cyclic unit of the Great Dyke contain several zones of sulfide mineralization. Zone 1, the Main Sulfide Zone (MSZ), consists of multiple overlapping zones, occurs at the top of the main bronzitite layer and consists of disseminated pyrrhotite, chalcopyrite, pentlandite and pyrite, increasing from about 2 percent at the axis to 6 percent near the margin. Sulfide Zones 2 and 3 are more attenuated than Zone 1 and extend over up to 80 m, but they contain < 1 percent sulfide.

Essential features of the mineralization include:

1) Pt, Pd and Au in sulfide underlying each sulfide zone increase as the zone is approached.

2) Pt, Pd and Au in sulfide drop sharply upwards into each sulfide zone, Pd more sharply than Pt, and both much more sharply than Au.

3) Pd/(Pd+Pt) thus drops sharply just above the base of a zone and Au/(Au+Pt) increases across a zone.

4) Cu in sulfides remains constant, thus Cu/(Cu+1000 x Pt) rises sharply to a value of 0.8–0.9 at the base of a zone.

5) Pt and Pd in sulfides remain low in any given zone, but at the top of a zone both start increasing; Pd/(Pd+Pt) rises rapidly to about 0.6 and Cu/(Cu+1000 x Pt) declines gently to level out between 0.2 and 0.4.

6) The base of each sulfide zone corresponds closely with a maximum in the Mg# of bronzite.

The systematic upwards decrease in Pd, Pt and Au in the sulfides of a zone can be explained as the consequence the fractionation of liquid sulfide from volumes of magma, with the partition coefficients decreasing in this order. A very reasonable match is obtained between observations and the calculations for the trends of absolute metal concentrations in both sulfides and rocks and the trends of metal ratios by modeling the behaviour of Pd, Pt, Au and Cu for simple Rayleigh fractionation using partition coefficients of $10^{4.5}$, 10^{4}, $10^{3.5}$ and 250 respectively. It is suggested that normal crystallization resulted in sulfide saturation of the magma and thus the initiation of sulfide zones 2 and 3, that mixing with primitive magma caused the cessation of sulfide segregation in each case and the replenishment of the PGE. Sulfide zone 1 is thought to have been induced by the mixing between less and more fractionated resident magma, the latter coming from the flanks of the intrusion.

1.3

PLATINUM MINERALIZATION IN THE MUNNI MUNNI LAYERED INTRUSION, PILBARA BLOCK, WESTERN AUSTRALIA.

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The 2.8 Ga Munni Munni Complex occupies an elliptical 9 by 25 km area, the southern half of which is covered unconformably by a 2.7 Ga volcanic sequence. The Complex consists of a lower 1850 m thick Ultramafic Series (UMS) and an upper Gabbroic Series (GS) at least 3000 m thick, and is in the form of an elongate funnel. The UMS is made up of macrorythmic cycles of dunite, wehrlite and clinopyroxenite, while the GS shows an uninterrupted fractionation trend from pigeonite gabbros through pigeonite – magnetite gabbros to granophyres. The base of the GS is very sharp, and marked by simultaneous appearance of cumulus plagioclase and pigeonite. At the top of the UMS is a distinctive 30 m layer of porphyritic orthocumulate websterite, which continues up the side walls as a marginal zone in contact with progressively more fractionated gabbros. A pyroxenite dyke intersects the sloping floor of the intrusion at a level close to the top of the UMS, and appears to have fed the websterite layer and the GS.

Cu-rich magmatic sulphides are weakly disseminated throughout the websterite, increasing in abundance to 1–3% in a semi-continuous layer a few metres below the gabbro. This layer extends over 8.2 km, averages 2.5 m in thickness, and has an average grade of 2.9 g/t Pt+Pd+Au, 0.2% Ni and 0.3% Cu with local higher grade zones. Peak PGE grades show very sharp upper cut-offs, and are commonly offset by about 1 m below the peak Cu and Ni grades, a feature common to the main PGE horizon of the Great Dyke which also shares a very similar stratigraphic position. PGE grades become lower and more widely dispersed further away from the intrusion walls. PGE-enriched sulphides also occur close to the websterite–gabbro contact where the websterite occupies a marginal position on the side wall.

Microprobe data on cumulus pyroxenes indicate that the websterite crystallized from a mixture of a relatively Mg and Cr rich "M" magma, parental to the Ultramafic Series, and an Fe-rich, strongly Cr-depleted gabbroic "G" magma. Pyroxenes from the PGE horizon are very low in Cr, suggesting that they crystallized from a "G"-rich hybrid.

The websterite formed as a result of an influx of dense "G" magma which ponded on the floor of the chamber. Crystallization of websterite occurred where the interface between the lower dense hybrid liquid layer and the upper, hotter "M" magma abutted the sloping floor and walls of the intrusion. As influx continued the level of the interface rose, and the websterite layer transgressed progressively up the wall. The upper few metres of the websterite, including the PGE-rich sulphides, accumulated during a period of quiescence at the end of the influx phase. Subsequent closed system crystallization produced the Gabbroic Series.

1.4

THE GEOLOGY AND PGE MINERALIZATION OF THE WONDINONG SEQUENCE, WINDIMURRA COMPLEX, WESTERN AUSTRALIA

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The Windimurra Complex is a large (80 x 30 km) layered mafic igneous intrusion, 2800 m.y. in age, which lies 500 km northeast of Perth in the Yilgarn craton of Western Australia. The lower section of the stratigraphy is exposed in the Wondinong area in the northwestern part of the Complex. The Wondinong sequence, which is approximately 5000 m thick, has been subdivided based on the cumulate sequence and whole-rock mg value (atomic % 100 x Mg/Mg+Fe^t), into five principal divisions: Gabbronorite, Anorthosite I, Norite, Anorthosite II, and Troctolite series. Two zones of platinum-group element (PGE) mineralization have been located within the 1200 m thick Norite series. Zone A mineralization ranges up to 2 m in thickness, and is associated with massive and disseminated chromite at the base of a 5 m thick dunite layer. Lenses of chromitite up to 0.3 m thick within this zone host erratic high-grade mineralization which has assayed up to 8.2 ppm PGE. The chromitite contains the platinum group minerals sperrylite, cooperite, and a range of Pt–Pd–Os–Ir–Rh species. Zone B mineralization lies 50 m stratigraphically above zone A mineralization, and is associated with disseminated sulphide (0.5%) within a 0.8 m thick layer of pegmatoidal leucocratic norite. This zone has assayed up to 1.7 ppm PGE. PGE concentration is interpreted to have resulted from the interaction of a new pulse of PGE-enriched sulphur-undersaturated magma with a more fractionated sulphur-saturated resident magma.

1.5

PLATINUM-GROUP ELEMENT MINERALIZATION IN THE LONGWOOD IGNEOUS COMPLEX, NEW ZEALAND

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The Longwood Igneous Complex is situated at the southern tip of the South Island of New Zealand. The Complex is some 32 km long and up to 12 km wide and is part of a more extensive north-trending belt of Permian volcanic, volcaniclastic and intrusive rocks.

Although the Complex is poorly exposed, four main rock associations can be recognised:

(i) Pahia Layered Series – an extensive gabbro sequence exhibiting the characteristic features of layered intrusions.

(ii) Marginal Diorite Series – a complex series of massive and xenolithic diorite/monzo-diorite rocks related to the layered series.

(iii) Pourakino Granodiorite – a large sodic granodiorite stock.

(iv) Granitoids – a number of small granite intrusions.

A two year exploration programme located significant platinum-in-drainage anomalies and went on to define a 10 km x 1 km source area of largely plagioclase-rich olivine-bearing cumulates within the layered series. Platinum-group element mineralisation in float rocks and significant platinum-in-soil anomalies have been found within this zone. Lithologies exposed near the mineralisation-in-float rocks are similar in modal composition and mineral chemistry to the anorthosite-troctolite-olivine gabbro associations within the Banded Series of the Stillwater Complex. The mineralised rocks are leucocratic plagioclase-olivine adcumulates with minor clinopyroxene oikocrysts and sparse (<0.5%) sulphides. Sulphides are pyrrhotite, chalcopyrite, pyrite and secondary copper sulphides. Cooperite, sperrylite, osmiridium, isoferroplatinum and plat- and palladoarsenide grains have been found in alluvial deposits derived from the complex. The normalised precious metal content of the mineralised rocks is similar to known economic mineralisation [(Pt + Pd)/S x 10^3 = 70–100] and highlights the potential for a large stratiform platinum-group element deposit in the Complex.

1.6

THE PLATINUM MINERAL POTENTIAL OF THE DUFEK COMPLEX, ANTARCTICA

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The Dufek (greater than 50 000 km^2) and Bushveld (65 000 km^2) Complexes are the two largest layered intrusions on the Earth by an order of magnitude. A comparison of the tectonic setting, geology and petrology of these two mega-intrusions indicates a number of significant similarities and differences.

The Dufek Complex (DC) intruded the edge of a transtensional intra-continental rift which developed during the initial break-up of Gondwana. There is increasing evidence that the Bushveld Complex (BC) was intruded in a similar tectonic setting. The ca 7–9 km thick DC compares well to the eastern BC. DC equivalents of the lower Main Zone (gabbro-noritic rocks) and Upper Zone (ferro gabbro-noritic rocks) of the BC are exposed in the Dufek Massif and Forrestal ranges which are separated by an unexposed 3 km thick succession which is equivalent to the Main Zone of the BC. Geophysics indicates that a further 1.8 to 3.5 km of unexposed Lower and Critical Zone type rocks occur below the Dufek massif section. The DC succession contains mineralogical and geochemical reversals similar to those of the BC. This strongly suggests that the chambers of both complexes were periodically replenished with fresh magma. These replenishments may have resulted in a Merensky type PGE deposit.

Both the Bushveld and Dufek magmas were derived from a relatively enriched source as indicated by the relatively high initial Sr-isotope ratios of both intrusions and their parental magmas. Comparison of the chemistry of the layered rocks, and possible parental magmas, indicates that the DC magmas were more CaO rich than those of the BC, and always had augite as a liquidus phase. Consequently thick chromitite layers which are prominent in the BC are inferred to be absent in the DC. Chromitite hosted PGE deposits such as the UG2 are therefore unlikely to occur in the DC.

On the basis of stratigraphic, geochemical and petrological similarities and differences we believe that there is a better than even chance of a sulfide based Merensky type PGE deposit in the Dufek Complex, the main detracting factor being our inferred lack of chromite in the succession.

1.7

THE ROLE OF SULPHUR CONTAMINATION IN MAGMATIC CU–NI–PGE MINERALIZATION IN THE CRYSTAL LAKE INTRUSION, THUNDER BAY AREA, ONTARIO

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The Crystal Lake gabbroic intrusion (1.1 Ga) is a small, unmetamorphosed, canoe-shaped layered intrusion of continental flood basalt affinity that is related to the Duluth Complex, and contains two distinct types of magmatic Cu–Ni–PGE mineralization.

Disseminated interstitial sulphides (pyrrhotite > chalcopyrite + pentlandite) are most abundant in the

Lower Unlayered Zone (LUZ, 60–90 m thick), a medium-grained to pegmatitic xenolith-rich plagioclase±olivine orthocumulate immediately above the basal contact zone. This mineralization constitutes the low grade Great Lakes Nickel deposit (40 Mt, 0.40% Cu, 0.20% Ni). Total Platinum Group Elements (PGE) in 100% sulphide = 29 ppm, and the PGE profile has a moderate positive slope, Pt/Ir = 40 (*Naldrett, 1981*). Most of the PGE and base metals correlate well with each other, but only Co correlates with S. Sulphur isotope and Se/S ratios correspond closely to those of the underlying Aphebian pyritic shales.

Sparse disseminated sulphides (mainly chalcopyrite and cubanite) in the overlying Cyclic Zone (CZ, about 40 m thick) are associated with thin (1 to 10 cm) chrome spinel-rich horizons in olivine gabbro and troctolite layers having ad-, meso-, and orthocumulate textures. Total PGE in 100% sulphide are higher (133 ppm), and the slope of the PGE profile is shallower (Pt/Ir = 11), compared to those of the LUZ. Cu, Ni and Pd correlate with S, while Os, Ir and Ru correlate with Cr. Sulphur isotope and Se/S ratios approximate mantle values, in sharp distinction to those of the LUZ.

These contrasting characteristics are largely explained by derivation of the S in sulphides of the LUZ through assimilation of pyritic shale in the mafic magma, whereas S in the CZ may be mainly of mantle origin.

1.8

PLATINUM METALS IN THE PROCESSES OF MAGMATIC SULFIDE ORE FORMATION: A REVIEW WITH SPECIAL REFERENCE TO THE ORIGIN OF SULFIDE-POOR DEPOSITS

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Magmatic sulfide platinum-copper-nickel deposits are subdivided into two ore groups, one including sulfide-rich deposits, the other – sulfide-poor or low-sulfide deposits. The behaviour of platinum metals in the processes of ore formation in these deposits may be considered on the basis of an equilibrium distribution of platinum metals in a pseudo-ternary system including a silicate melt, an immiscible sulfide liquid and the coexisting fluid. In evolving ultramafic-mafic magmas the highest solubility of platinum metals is achieved under high parameters in an immiscible sulfide liquid proportionally to the value of the chemical affinity of each platinum metal to sulphur. Maximum solubility is achieved for ruthenium, osmium, iridium and rhodium, minimum - for platinum. The study of abyssal xenolites of kimberlites showed that considerable solubility of platinum in sulfide melt occurs at mantle parameters. Sulfide liquid crystallization in a magmatic chamber leads to the formation of solid solutions of platinum metals, primarily in monosulfide solid solutions and later in products of their solid phase transformations in a subsolidus. Solid solutions of platinum metals in sulfides are the dominant type of their state in non-metamorphosed deposits. The composition, the conditions of the evolution of the sulfide liquid and coexisting fluid phase as well as the disturbance of the equilibrium between them in the region of the sulfides subliquidus determine the species variety and the sequence of palladium and platinum mineral deposition. Replacement of binary and ternary alloys by intermetallids, arsenides and sulfides of palladium and platinum, as well as the emergence of minerals of other platinum metals depends on the evolution of parageneses of magmatic sulfides.

It is shown that sulfide-poor (low-sulfide) deposits of platinum metals which until recently have been restricted to the respective horizons in Bushveld and Stillwater complexes, commonly occur in ultramafic-mafic massifs varying in composition and structure. The composition and inner structure of low-sulfide platinum-bearing horizons depend on petrological peculiarities of intrusives. The formation of low-sulfide deposits is associated with the process of the interchamber differentiation of the magmatic system and with the redistribution of platinum metals into a fluid coexisting with the melt.

1.9

MINERALOGIC AND ISOTOPIC STUDIES OF PLATINUM-GROUP ELEMENT MINERALIZATION AT THE BABBITT Cu–Ni DEPOSIT, DULUTH COMPLEX, MINNESOTA

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The Babbitt Cu–Ni deposit consists of disseminated and massive sulfide mineralization located within troctolitic and gabbroic rocks of the Duluth Complex, and locally within pelitic hornfels of the underlying Virginia Formation. At least four periods of sulfide mineralization have been identified, based on spatial, textural, mineralogic, and isotopic characteristics. Platinum-group element abundances in basal zone mineralization range as follows (ppb): Os, 3–32; Ir, 0.6–29.9; Ru, 4–101; Rh, 1–101; Re, 2–220, Pt, 3–3000; Pd, 19–1100. Ir, Os, Ru, Rh, and Re show strong interelement correlations, and a moderate correlation with S (r = 0.7). This group has behaved as relatively immobile elements, and their distribution is related to primary magmatic processes. Pt and Pd, however, show very different behaviour, exhibiting poor correlations with each other, as well as other PGE, Cu, Ni, and S. Both Pt and Pd have been remobilized during hydrothermal alteration.

A PGE-enriched zone at Babbitt has been detected that is spatially removed from the area of highest grade Cu–Ni ore. The enriched zone is characterized by the presence of abundant bornite, an increased proportion of chalcopyrite, Zn-bearing hercynitic spinel, and anomalously low and variable $\delta^{34}S$ values (-1.4 – 7.9 ‰) relative to the higher grade Cu–Ni ore. Synchroton X-ray fluorescence microprobe analyses reveal ppm (16–132) quantities of Pd in cubanite, chalcopyrite, and maucherite ($NiAs_2$) from high bulk Pd samples, and Pd-enrichment in mackinawite produced during hydrothermal alteration. Sperrylite has been the only Pt-bearing mineral identified thus far. An 0.1 to 0.2 mm cubic grain of sperrylite is capable of supplying all the Pt contained in most fire assay samples. However, Pt values do not correlate strongly with As (2 – 134 ppm), which also occurs in maucherite and niccolite, and as a trace constituent in several sulfide minerals. Although biotite and apatite throughout the basal zone at Babbitt are relatively Cl-rich (0.1 – 0.7 and 0.9 – 1.3 wt.%, respectively), no direct relationship between PGE-enrichment and Cl-rich minerals has been established. Fe-rich chloritic material that occurs as veinlets in sulfide-bearing samples contains in excess of 0.4 wt.% Cl, and attests to the Cl-rich nature of late stage fluids. Data are most consistent with a model whereby the PGE-enriched zone represents a distinct intrusive phase in the basal portion of the Duluth Complex, but that Pd and Pt have been selectively mobilized during late-stage hydrothermal alteration.

1.10

PLATINUM GROUP ELEMENTS IN ANORTHOSITIC ROCKS OF THE DULUTH COMPLEX, MINNESOTA, USA

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Platinum group element (PGE) concentrations of whole-rock, plagioclase, and interstitial mafic mineral fractions of minor sulfide-bearing anorthositic series rocks from the Duluth Complex, Minnesota, U.S.A., are being determined using the nickel sulfide fire assay/neutron activation method. Pd/Ir ratios of two anorthositic samples are lower than those found in the J-M Reef and in fractionated, sulfide-bearing troctolitic rocks of the Duluth Complex (Minnamax); but are greater than the Pd/Ir ratios of the UG-2, the Merensky Reef, Talnakh and less-fractionated, spinel-bearing gabbroic rocks in the Duluth Complex (Duval) (Figs. 1 and 2).

Duluth Complex anorthositic rocks are a product of fractionation of chrome spinel, olivine, plagioclase, and clinopyroxene from tholeiitic magmas at pressures of 8-10 kb (*Miller, 1986*). *Naldrett and Barnes (1986)* have suggested that sufficient Ir may partition into chromite and olivine to affect Pd/Ir ratios of basaltic melts in which olivine fractionation occurs (Fig. 2). If this model is correct, then the limited data on Duluth Complex rocks can be interpreted as follows: 1) the Duval sample, a chrome-spinel, ilmenite, plagioclase and high-Mg olivine cululate with low Pd/Ir ratios, could represent the segregated portion of a primitive magma; 2) anorthositic gabbro BL-27 could be a plagioclase crystal mush which trapped moderately fractionated melt; 3) the Minnamax sample could be a product of more extensive chrome-spinel and olivine fractionation. The ore grade concentrations of platinum group elements in the Duval sample would require invoking the mixing model of *Campbell et al. (1983)*.

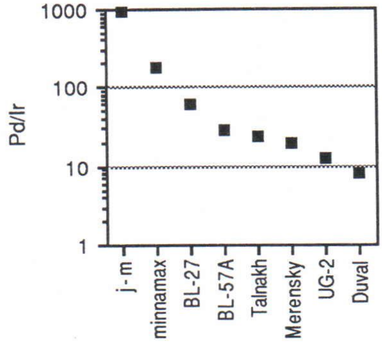

Figure 1. Pd/Ir Ratios for Duluth, Bushveld, and Stillwater Complexes, and Talknakh. BL - Duluth Complex anorthositic rocks; Duval and Minnamax - Duluth Complex troctolitic rocks.

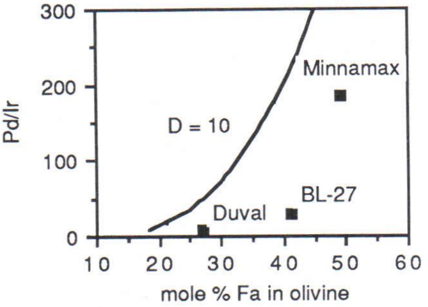

Figure 2. Pd/Ir vs. Mole % Fa in Duluth Complex Troctolitic and Anorthositic Rocks. Line represents modelling of fractional crystallization of basaltic composition, using distribution coefficient D (mafic silicate/silicate melt) = 10 (from Naldrett and Barnes 1986). If Fa and Pd/Ir increase with fractionation, then anorthositic rocks appear to have undergone intermediate amounts of fractionation, or have trapped intercumulus liquid of intermediate composition.

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1.11

GEOCHEMICAL AND ISOTOPIC CONSTRAINTS ON THE GENESIS OF THE MONTCALM GABBROIC COMPLEX AND NI–CU DEPOSIT, WESTERN ABITIBI SUBPROVINCE, ONTARIO, CANADA

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Microprobe and geochemical traverses across a 500 m section, from the basal Pyroxenite Zone (PZ, 0 m–170 m) through the Gabbro Zone (GZ, 170 m–500 m) which hosts the Montcalm deposit (3.6 million t 1.4% Ni, 0.7% Cu), provide constraints on the genesis of the Montcalm Gabbroic Complex (MGC) and Ni–Cu deposit. In the PZ, there is an increase toward the base in whole rock incompatible element and FeO contents, and in orthocumulus phases, whereas cpx Mg numbers (corrected for minor sulfide) remain constant at 78–82. This basal reversal is interpreted as post-cumulus, downward fractionation of intercumulus liquid from the base of the mesocumulate GZ. In the GZ, trace element decoupling from major element trends are noted, with two upward LREE-enrichment trends not accompanied by significant variation in cpx or whole rock Mg numbers. These occur across the PZ–GZ contact, and within the GZ at 290 m to 320 m, and may represent LREE-enrichment of intercumulus liquid during post-cumulus fractionation, with the Mg and Fe buffered by cumulus pyroxene. A steady increase in whole rock Mg numbers from 170 m to 330 m may reflect constant addition of more primitive magma into the chamber. Whole rock ε_{Ndt} values corrected to a U–Pb age of 2702 ± 2 Ma range from +3.8 for PZ chill to +2.4 – +2.8 for GZ rocks to +1.0 for an upper Ferroan Gabbro Zone (FZ) sample. These data indicate progressive contamination of an isotopically depleted, mantle-derived magma for the MGC during emplacement and crystallization by an older, enriched crustal component. Indirect evidence for older crust is found in nearby regional granitoids, which show signs of zircon inheritance at >2900 Ma, and have ε_{Ndt} values of +0.6 and – 0.4 with T_{DM} model ages of >3 Ga.

In the PZ, Ni, Cu and Au contents and their sulfide-normalized values increase with height, then decrease dramatically near the PZ– GZ contact. RNAA data for selected rocks indicate that although PZ rocks have low abundances in PGE+Au, they are significantly enriched in these elements in comparison to GZ rocks. These observations support earlier hypotheses that the PGE-poor Ni–Cu deposit formed after (PZ) fractionation that included continual sulfide removal from a picritic parent liquid, and that the deposit was emplaced tectonically into its present location during or shortly after GZ consolidation during the late Kenoran Orogeny. Contamination by an older crustal component, either within the magma chamber or at lower crustal depths may have played an important role in sulfur saturation and the formation of the Ni–Cu deposit.

1.12

ASSOCIATION OF PLATINUM-GROUP MINERALS IN A LAYERED INTRUSIVE OF NORTH KARELIA

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A layered intrusive of the Early Proterozoic age (2400 million years ago) is composed of a petrological series of rocks forming a unique row from peridotites to quartz-bearing gabbronorites. The regular layering of the massif was disturbed by later bodies of massive and poikilophitic micro-gabbronorites confined to the zone of development of olivine gabbronorites. Disseminated sulfide-platinum mineralization occurs in gabbronorites and anorthosites of the exocontact of micro-gabbronorites as well as in the bodies of micro-gabbronorites containing schlieren-like segregations and veins of pegmatoid plagiopyroxenites differently enriched by sulfides.

In gabbronorites and anorthosites platinum-group minerals (PGM) are localized among rock-forming silicates and in pyrrhotite-pentlandite-chalcopyrite aggregates associated also with chalcocite, cobaltite-gersdorffite, polydymite, galena and sphalerite.

PGM association is represented by sperrylite, hollingworthite, mertiite, isomertieite, mayakite, palladoarsenide, stillwaterite, merenskyite, kotulskite and mineral $(Pd,Ag,Cu)_4S_3$, sometimes intergrown with native gold. Together with rhodium, palladium forms solid solutions in pentlandite and cobaltite.

PGM association in pegmatoid plagiopyroxenite from micro-gabbronorites is connected with millerite-bornite-chalcopyrite (magnetite, godlevskite, clausthalite) and pentlandite-chalcopyrite mineralization. A typomorphic paragenesis of these rocks is represented by bismuth-tellurides of palladium and silver-telargpalite, sopcheite and previously unknown Pd_6AgTl_4, $(Pd,Ag)_8Tl_3$ forming intergrowths with moncheite, kotulskite, tulameenite, $(Pd,Sn,Cu,Fe)_5(Tl,S)_2$ as well as hollingworthite, irarsite, mertieite, taimyrite, $Pd_2(Sn,Sb)$, michenerite and hessite.

The formation of sulfide and PGM associations in micro-gabbronorites is connected with their crystallization from the latest portions of the sulfide-silicate melts saturated by a fluid phase and with partial recrystallization of micro-gabbronorites with the formation of platinum-bearing pegmatoid pyroxenites.

1.13

PETROLOGY AND PGE MINERALIZATION OF THE EARLY PROTEROZOIC LAKE OWEN LAYERED MAFIC INTRUSION, SOUTHERN WYOMING, USA

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The Lake Owen Complex (LOC) is the easternmost and smallest of three synorogenic, layered gabbroic intrusions in the 1770–1785 Ma-old Green Mountain accreted arc terrane of southern Wyoming and northern Colorado. Unlike the nearby Elkhorn and Mullen Creek gabbroic complexes, the Lake Owen Complex is virtually undeformed and unmetamorphosed. The intrusion is of crude funnel or bowl form – the lowest cyclic unit has a strike length of about 3 km, succeeding cyclic units on-lap the gneissic floor rocks, and the uppermost cyclic units have a strike length of about 12.5 km. The LOC is tilted at an average dip of ca. 75° to expose a layered sequence containing at least 18 cyclic units defined by large-scale repetitions of two or more units in the lithologic sequence: troctolite → olivine gabbro → gabbronorite → Fe–Ti oxide gabbronorite, and by cyclic variation of plagioclase composition over the range An_{82-52} and of olivine and orthopyroxene composition over the range Mg# 84–50, determined by electron microprobe analyses of 175 samples traversing the layered sequence.

Cumulus sulfide mineralization occurs in at least 12 stratigraphic horizons. Four contain PGE +Au mineralization at grades > 1ppm. Cumulus sulfide (mainly pyrrhotite, pentlandite, and chalcopyrite ± PGE minerals) in olivine-bearing rocks near the base of three cyclic units was precipitated during renewed magma introduction into the chamber. In such units, modal layering and mineralization are lensy and discontinuous. The second principal lithologic association of cumulus sulfides is with titanomagnetite cumulates near the tops of cyclic units; in most of these occurrences, cumulus sulfide saturation immediately preceded or immediately succeeded onset of cumulus titanomagnetite precipitation. Magnetite saturation occurred at oxygen fugacities near or above the experimental nickel–nickel oxide buffer. Under such conditions, much of the sulfur in the magma is sulfate, and the intimate association of titanomagnetite and sulfide liquid precipitation is due to operation of a chemical feedback loop involving sulfur and iron redox couples in the magma, such that sulfide precipitation before magnetite oxidizes the magma and promotes prompt magnetite saturation and precipitation; or magnetite saturation before sulfide (in other units) reduces the magma, converting sulfate to sulfide, and promotes prompt saturation of cumulus sulfide liquid. In two units in which cumulus sulfide saturation is associated with cumulus titanomagnetite, the mineralization consists of the unusual assemblage bornite + chalcopyrite + carrollite +

millerite + Ti-poor magnetite ± PGE minerals (moncheite, merenskyite, michenerite, cooperite) ± Au–Ag–Pd alloys in pink-labradorite gabbronorite that generally is devoid of hydrothermal effects. Pyrrhotite, pyrite, pentlandite, or other Fe-rich sulfides are absent from this assemblage, and bornite may greatly exceed chalcopyrite in abundance. In one unit, stratiform bornite-rich mineralization of this type, with ppm-level Au + Pt + Pd, is continuous for at least 2 km, and in another cyclic unit bornite-rich mineralization extends over a strike interval of at least 10 km. We interpret the stratiform bornite-magnetite-rich mineralization to have developed by segregation of an immiscible oxy-sulfide liquid with atomic O>S. Most Fe in this immiscible ore liquid crystallized as magnetite. It is interesting that such an unusual liquid apparently may be an efficient collector of precious metals.

1.14

MAGMATIC PGE–Cu–Ni SULFIDE MINERALIZATION, PETROLOGY, AND STRUCTURE OF THE EARLY PROTEROZOIC MULLEN CREEK LAYERED MAFIC-ULTRAMAFIC INTRUSION, MEDICINE BOW MOUNTAINS, WYOMING, USA

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The Mullen Creek layered mafic-ultramafic igneous complex has an exposed stratigraphic thickness of about 8.5 km, strike lenth of ca. 41 km, and an outcrop area of about 200 km^2. The intrusion was emplaced 1778±2 Ma ago (zircon U–Pb; Loucks et al., 1988, GSA Abs., v. 20) into almandine-amphibolite-grade supracrustal gneisses at a pressure of 5.3±0.6 kb and depth of ca. 19 km (at the base of the intrusion) in an island arc tectonic setting. Shortly after or possibly during late stages of crystallization, the complex underwent severe deformation, at which time the northwestern margin of the complex was tectonically juxtaposed against Archean gneisses of the Wyoming craton, and shear along the mylonite belt suture zone drag-folded the sill-like layered succession as a closed, synclinal, U-shaped fold. Igneous strata now have dips of 80–90° throughout most of U-shaped intrusion. The igneous stratigraphy is displaced and hydrated along many second-order faults splaying southeastward from the mylonite belt.

On the basis of petrography and ca. 240 whole-rock chemical analyses along traverses spanning the entire layered sequence, at least a dozen major cyclic units have been defined by cyclic variation of chemical differentiation indices and repetitions of lithologic sequence. The succession of layered mafic and ultramafic rocks has been divided into three major units, each of which consists of multiple cyclic units: the Lower Series, the Jays Roost Series, and the Upper Series. In the Lower and Upper Series, orthocumulate bronzitite or harzburgite is developed dicontinuously along the base of most cyclic units. These grade upward through fine-grained, poorly layered gabbronorite and magnetite-gabbronorite to hornblende-cumulate gabbro and hornblende-biotite-quartz diorite. The compositions of ultramafic rocks at bottoms of cyclic units indicate very magnesian cumulus olivine and orthopyroxene ($Mg/Mg+Fe \approx 0.92–0.86$) and suggest derivation of both the Lower Series and Upper Series from a boninitic or relatively siliceous, hydrous, high-magnesium tholeiite parent magma type. In contrast, the Jays Roost series consists of modally banded, coarse-grained leucotroctolite, anorthosite, leucogabbro, gabbronorite, and Fe–Ti-oxide-cumulate ferrogabbro that appear to be products of a less hydrous, high-alumina-tholeiite magma type.

The Lower Series contains cumulus sulfide mineralization in harzburgite or chromite-harzburgite at the base of several cyclic units, including significant Pt and Pd concentrations at the New Rambler mine. Sulfide ore averaging ≈160 ppm precious metals in 100% sulfide, $Pd+Pt/\Sigma PGE >.99$, and $Cu/Cu+Ni >.98$ occurring in dislocated, tectonized gabbroic rocks at the New Rambler mine has previously been interpreted as hydrothermal in origin, but is shown here to be magmatic. Igneous textures, the peculiar chemical composition, and structurally discordant nature of the New Rambler mineralization can be reconciled by a genetic model in which compositionally evolved, residual, interstitial sulfide liquid was tectonically mobilized (filter pressed) out of a mineralized, feldspathic, pegmatitic harzburgite source stratum and injected into underlying, mushy gabbroic cumulates, probably during collision of the island arc with the craton. Portions of these structurally discordant orebodies were tectonized by subsolidus deformation along strands of the tectonic suture mylonite belt.

1.15

NICKEL-COPPER AND PLATINUM-GROUP ELEMENT MINERALIZATION ASSOCIATED WITH THE JINCHUAN ULTRAMAFIC INTRUSION, NORTHWEST CHINA

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The dyke-like Jinchuan ultramafic intrusion (1509 my K–Ar age) hosts PGE-rich nickel-copper sulphide mineralization and represents the only actively producing PGE deposit in China. The deposit is located in the Gansu Province, northwest China and is situated within the rift belt of the southwest margin of the Sino-Korean craton. The intrusion was emplaced into Archaean gneisses, marbles and migmatites, and comprises an assemblage of dunites, lherzolites, harzburgites and olivine-websterites. It has a strike length of approximately 6500 meters and a width of 20–520 meters.

The intrusion contains several hundred nickel sulphide ore bodies found in the following geological settings.

1. Basal massive ore bodies hosted in dunites which are the most important nickel ore type.
2. Hangingwall disseminated ore bodies, where sulphides occur interstitially in a matrix of olivine and pyroxene crystals.
3. Massive vein ore bodies, which are confined to fracture zones.
4. Contact metosomatic ore bodies, which are associated with the footwall marbles or with xenolithic rocks.

PGE are present as a minor but significant component of the sulphide ores and are preferentially associated with copper-rich sulphides. PGE occur mainly as arsenide, telluride, tellurobismuthide and antimonide minerals. Generally, the PGE values display strong fractionation in their chondrite-normalized distribution patterns and show similar geochemical characteristics to those associated with layered complexes. The genesis of the mineralization is influenced by country rock contamination as well as late-stage magmatic fluids.

1.16

THE GEOLOGY AND STRATIGRAPHIC SETTING OF THE WEDZA–MIMOSA PLATINUM DEPOSIT, GREAT DYKE, ZIMBABWE

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The Wedza–Mimosa Pt deposit is a narrow layered stratiform zone (Main Sulphide Zone, MSZ) of PGE-bearing sulphide pyroxenite. This poster describes the features of the MSZ and the highly complex stratigraphy of the host rocks. Principal themes are the systematic transverse variations of both the MSZ and the host rock lithology, together with evidence for discordant layering relationships. These features are interpreted in terms of the high transverse heat flux and heat gradient imposed by the narrow elongate funnel-shape of the original magma chamber and their effects on the crystallisation rate, the sequence, timing, composition and proportions of liquidus phases, the incompatible element content of the residual magma, S solubility, the R factor and partition coefficients. Significant longitudinal stratigraphic variations also point to gradients in the physical and chemical state of the magma along the length of the magma chamber that were probably controlled by variations in magma mixing, and in the aspect ratio of the magma chamber, as well as wall rock irregularities.

1.17

HARTLEY PLATINUM PROJECT, ZIMBABWE

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The Hartley Platinum Project is a proposed 2 million tpy underground mining project which will recover platinum, palladium, rhodium, iridium, gold, nickel, copper and cobalt from the Main Sulphide Zone (MSZ) within the Hartley Complex in the Great Dyke of Zimbabwe.

The Great Dyke is a 530 km linear Proterozoic mafic-ultramafic intrusion which transects Zimbabwe in a north-northeasterly orientation. Where it transects Archaean granitoids the Dyke is generally less than 2 km wide. Where it transects Archaean greenstone belts the Dyke widens out into elongated lopolithic layered complexes.

The Hartley Complex is approximately 95 km long and has a maximum width of 11 km. The Complex has an ellipsoidal canoe-shape with layering dipping gently towards the axis. The exposed sequence of rocks, from bottom to top comprises: (i) dunite with chromitite layers, (ii) harzburgite, (iii) bronzitite, (iv) websterite and (v) gabbro and norite.

The MSZ is a zone of disseminated sulphides conformable to layering, which is hosted within bronzitite below the main websterite unit and 20 metres below the gabbro which marks the top of the ultramafic sequence. The MSZ is 1.5 to 2 metres thick with a sulphide content between 2 and 5 volume percent. The principal sulphide minerals are pyrrhotite, pentlandite, chalcopyrite and pyrite.

Within the MSZ, nickel and copper values increase gradually downwards to a peak of 0.5% Ni and 0.35% Cu and then decrease sharply. Peak values for the platinum-group elements (PGE) and gold are stratigraphically below the nickel-copper peak. However, the PGE and gold values increase sharply to peak values and decrease gradually downwards. Typical peak values are 7.5 g/t Pt, 3.5 g/t Pd, 0.36 g/t Rh, 0.28 g/t Ru, 0.1 g/t Ir and 1.5 g/t Au.

Delta Gold N.L. has estimated a resource within a 12 km x 2 km portion of the Complex of 120 million tonnes grading 2.7 g/t Pt, 2.0 g/t Pd, 0.21% Ni and 0.14 % Cu over an average thickness of 1.3 metres. A feasibility study due for completion in August, 1989, is evaluating the project which would produce annually 100,000 ounces platinum, 84,000 ounces palladium, 10,000 ounces gold, 8,000 ounces rhodium, 2,700 tonnes nickel, 1,700 tonnes copper as well as small but marketable quantities of ruthenium, iridium and cobalt.

2. BUSHVELD COMPLEX

2.1

LATERAL VARIATIONS IN THE PGE BEARING UG2 CHROMITITES AS RELATED TO THE DISCONTINUITY BETWEEN THE SOUTHERN AND CENTRAL SECTORS OF THE EASTERN BUSHVELD COMPLEX

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The UG2 Upper Group chromitites in the Bushveld Complex are a major reserve of platinum group elements (PGE) but, up to present, mining has largely been restricted to the western side. Recent investigations reveal hitherto unknown major development of the UG2 in the Eastern Bushveld Complex, south of the NE trending Steelpoort Fault. This fault was generally considered to define a major break between the southern and central sectors of the Eastern Bushveld Complex, but the present study recognises a curvilinear EW trending discontinuity up to 3 km north of the Steelpoort Fault. The 'fault' is therefore entirely within the southern sector.

Magnetic, gravity and vibroseis surveys were used to delineate the boundary between the two sectors, subsequently confirmed by 45 boreholes drilled in an area of 6 km^2. The boreholes reveal major differences in lithologies, mineralization and stratigraphic thicknesses of units between the central and southern sectors, with the changes occurring over a boundary zone approximately 200 m wide. In spite of the differences, the lithostratigraphy is broadly comparable for the two sectors.

Differences in the characteristics of the chromitite layers between the two sectors are particularly striking. In the central sector the Lower Group chromitites are well developed and are of economic importance, whereas those of the Middle Group are narrow and uneconomic. The converse is true for the southern sector in which the Lower Group chromitites are poorly developed and the Middle Group chromitites are thick and are mined. The PGE bearing UG2 chromitites in the central sector occur as narrow (<5–60 cm thick) layers, separated by pyroxenite units up to 10 m thick. In the southern sector chromitites of this group are relatively thick (up to 1.4 m) and are economically viable for PGE. The PGE mineralization contained within the chromitites is significantly different for the two sectors in terms of concentrations and distribution patterns through the chromitites. Total PGE content is, however, remarkably similar for the two sectors indicating a similar source for the metals and enrichment process.

The interface between the southern and central sectors is significant, not only in terms of economic potential of the UG2 platinum bearing horizon, but also as regards evolution of the Bushveld Complex. It is envisaged that these sectors represent individual compartments, which underwent similar crystallization sequences but each retaining its identity because of small differences in magma composition and different conditions prevailing in each compartment.

2.2

THE SR-ISOTOPIC STRATIGRAPHY OF THE BUSHVELD COMPLEX: SIGNIFICANCE FOR MODELS OF PGE MINERALIZATION

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A comprehensive Sr-isotopic stratigraphy comprising the Lower (LZ), Lower Critical (LCZ), Upper Critical (UCZ), Main (MZ), Upper Main (UMZ) and Upper Zones (UZ) of the Bushveld Complex, with lateral extensions straddling the Merensky reef is now available. The LZ magmas precipitated harzburgite and had Sr-isotope initial ratios (R_O's) between 0.7055 and 0.7070. The orthopyroxenite dominated LCZ has *lower* R_O's of 0.7048 to .7055, and the noritic UCZ 0.7058 to 0.7064, but ratios as high as 0.7073 do occur in some samples. A major break occurs at the Merensky reef to higher ratios of .7075 to .7090 in the gabbronoritic MZ. A further abrupt break occurs at the Pyroxenite marker back to .7073 in the gabbronoritic to ferrogabbroic UZ.

The Lower, Critical and Lower Main Zone isotopic data indicate that this succession was dominated by numerous small additions of magma, with large influxes occurring at the top of LZ, at the boundary of the LCZ and UCZ, the base of the UG2 succession, and a very large influx at the UCZ–MZ boundary – the Merensky reef. This succession comprises the open system Integration Stage during which magma addition and differentiation were equally important. During the precipitation of the UMZ and UZ there was very little magma addition and except for the Pyroxenite marker position between the UMZ and UZ, this succession is the Differentiation Stage and is dominated by closed system crystal liquid fractionation.

The data also indicate that the PGE mineralization at the UG2 and Merensky reef is the result of mixing processes involving contrasting magmas at the liquidus stage leading to the precipitation of chromite and/or sulfide rich in PGE. Both the UG2 and the Merensky reef are associated with abrupt increases in R_O indicating the influx and mixing of fresh magma. In some cases (Amandelbult and Brits areas) the isotopic profile at the Merensky reef is step-like and upward infiltration of Sr- (and PGE) rich residua from the footwall cannot be invoked. This is in contrast to the Rustenburg and Union areas where upward infiltration probably did occur as suggested by Kruger and Marsh (1982).

These data suggest that PGE mineralization in the layered sequence is dominantly the result of magma influx and mixing and not upward infiltration of PGE enriched residua. The latter process was important in some areas in modifying the chemistry of the pegmatoid.

2.3

PETROGENESIS OF THE MERENSKY REEF

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A petrogenetic model for the Merensky reef and adjacent rocks in the Rustenburg section of the western Bushveld Complex has been developed based on detailed field and petrographic observations and mineral composition data. The model maintains that the reef formed by reaction of hydrous melt and a partially molten cumulate assemblage.

In all the measured sections of the reef, it has been found that the basal chromitite is separated from underlying norite by a cm-thick layer of anorthosite and that the thicknesses of the two layers exhibit a well-defined positive correlation. In one of the Merensky potholes, meter-size inclusions of the norite footwall exist within the pegmatitic reef. The inclusions are completely surrounded by zones of anorthosite and chromitite identical to the sequence at the base of the normal Merensky. The field relations preclude a cumulate origin for these zones and suggest that they and the basal layers of the reef represent a reaction front between two distinct melt compositions. Two additional observations are relevant. First, in nearly all samples of Merensky pyroxene-plagioclase pegmatoid, olivine exists as relict cores in orthopyroxene, implying that olivine was once much more abundant. Second, the pegmatoid locally contains cm- to m-size inclusions of fine-grained pyroxenite identical to the pyroxenite of the hanging wall, suggesting that the inclusions represent part of the protolith of the pegmatoid.

It is proposed that the present reef was originally the contact between partially molten norite footwall and pyroxenite hanging wall. Fractures in the cumulate pile below the present Merensky unit, probably at the loci of what are now potholes (e.g., 1), permitted upward migration of volatile fluid. The fluid became concentrated at the reef level because, in contrast to the underlying and overlying cumulates, the amount of partial melt there was sufficient so that brittle deformation could not be sustained. Experimental investigations (2,3,4) demonstrate that addition of water to basaltic melt expands the fields of olivine and chromite at the expense of those of orthopyroxene and plagioclase. The anorthosite and chromitite layers formed at the interface between anhydrous intercumulus melt in the footwall norite and hydrated melt in the present Merensky as the hydration front moved down into the footwall. Thus, as the intercumulus melt hydrated, cumulus orthopyroxene dissolved, the melt composition moved into the field of plagioclase stability and the anorthosite layer formed at the interface. With the addition of more water, plagioclase became unstable, the melt became chromite-saturated and the chromitite formed. Olivine also crystallized from the hydrous melt but reacted back to orthopyroxene with cooling. The model is consistent with computations of mass balance and with observed variations in mineral compositions.

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2.4

PLATINUM-GROUP MINERALS AS LIQUIDUS PHASES IN THE UG–1 CHROMITITE LAYER, BUSHVELD COMPLEX

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Samples of the UG–1 chromitite layer from the Bushveld Complex were investigated to determine the frequency and mineralogical composition of platinum-group minerals (PGM) included in chromite grains. Four types of inclusions were distinguished according to their mineralogical composition, viz., inclusions consisting (i) only of laurite, (ii) only one PGM other than laurite, (iii) of assemblages of PGM, and (iv) of PGM associated with base-metal sulphides (BMS). It was found that laurite is the dominant PGM enclosed by chromite and was observed in assemblages with metallic PGM, sulphides and sulpharsenides. This study indicates that PGM assemblages without BMS coexisted at magmatic temperatures as liquidus phases, whereas PGM associated with BMS were enclosed after immiscible sulphide melt had started to form. Under the assumption of increasing sulphur fugacity during chromite formation, the crystallization sequence of magmatic PGM began with Ru-rich alloys and laurite. Pt- and Pd-bearing PGM crystallized later from the silicate melt. The discrepancy in the frequency of Ru- and Pt-bearing magmatic PGM despite higher concentrations of Pt in the silicate melt compared to Ru indicates that the solubility of Ru in the silicate melt from which the UG–1 chromitite formed was much lower than the solubility of Pt. The formation of magmatic PGM and their Ru-dominance is not reflected in the whole rock PGE-pattern because immiscible sulphide melt scavenged the PGE remaining dissolved in the silicate melt and concentrated them together with the magmatic PGM enclosed by chromite to produce a whole rock PGE-pattern indistinguishable from a pattern produced by sulphide collection alone.

2.5

CONTRASTING Os/Ir-RATIOS OF CHROMITITE LAYERS, BUSHVELD COMPLEX – INDICATORS FOR DIFFERENCES IN PARENTAL MELT COMPOSITIONS

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In many ores and rock types, chondrite normalized PGE-patterns follow a positive slope with Os < Ir < Ru. However, in some types of deposits associated with certain rock types, the chondrite normalized pattern gives Os > Ir < Ru. The case in which Os > Ir in chondrite normalized pattern will be called a "*negative Ir-anomaly*".

Taking the chondritic values of Os and Ir (514 ppb and 540 ppb respectively) into account, an Os/Ir ratio of > 0.95 in the rock represents a negative Ir-anomaly. Accordingly, ratios of < 0.95 will be called "*positive Ir-anomaly*".

From the type of Ir-anomaly in different types of mantle melts it is concluded that low degrees of partially melting an undepleted mantle leads to a positive Ir-anomaly in the melt and a negative Ir-anomaly in the residuum. To explain the formation of positive Ir-anomalies in mantle melts representing low degrees of partial melting , a mantle mineralogy of the PGE in analogy to magmatic PGM in the Bushveld Complex is assumed. Arsenic-bearing Ir-rich PGM are considered to be dissolved in the partial melt in preference to alloys and sulphides. Ir is in this way depleted in the source and silicate melts from later melting events of depleted mantle will show a negative Ir-anomaly. It is highly unlikely that a negative Ir-anomaly can be enhanced or created after the silicate melt has left its source region. Therefore, the Os/Ir ratio reflects the source that is melted.

The role of chemically distinct parental magmas and their importance for the genesis os chromitite layers and the Merensky reef has repeatedly been emphasized. the data presented in this paper suggest that the PGE pattern of the MG and UG chromitite layers differ not only in their degree of fractionation but also in their Os/Ir ratios. A systematic relation between initial strontium isotope data and the Os/Ir ratio across the MG chromitite layers is indicated which implies that the parental melt with the higher Ro entering the Bushveld Complex at this stratigraphic level was also characterized by a high Os/Ir ratio. Because the silicate melt reached sulphur saturation repeatedly over this stratigraphic interval, the PGE-pattern is mainly controlled by the fresh magma. The formation of magmatic laurite does, however, permit a gradual "mixing" of the Os/Ir ratio.

Insufficient knowledge of the Os contents and Os/Ir ratios in different parental melts to the Bushveld Complex does not allow to establish exactly the relation between the Os/Ir ratio of chromitite layers and their parental silicate melts. It can, however, be postulated that the PGE-pattern of the UG–2 and the underlying chromitite layers were not derived from the same type of silicate melt.

2.6

PGE MINERALIZATION IN THE NORTHERN SECTOR OF THE EASTERN BUSHVELD COMPLEX

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Unusual facies of both the Merensky Reef and the UG–2 chromitite layer are developed in the northern sector of the eastern Bushveld. Within the ± 6 m thick basal pyroxenite of the Merensky cyclic unit, up to four mineralized layers can be developed which vary in thickness from 40 cm to 1.6 m. Several of these contain significant PGE mineralization with an increase in the Pt/Pd ratio upwards in the succession.

The UG–2 chromitite layer is sulphide-rich and frequently contains in excess of 0.5 wt per cent Ni + Cu. Towards the west, the reef thickens from a normal 1 m thick homogeneous chromitite layer to a 1.75 m thick layer of which the lower two thirds is in places coarse grained and sulphide-rich and the upper third fine-grained and comparatively sulphide-poor. Both parts of the layer are well mineralized, with mineralization often extending for some distance into the footwall rocks.

UG–2 intersections investigated so far clearly indicate that a PGE enriched immiscible sulphide liquid separated prior to or simultaneously with chromite crystallization. Within the sulphide-rich portion of the UG–2 reef the major base metal sulphides are pyrite, pentlandite and chalcopyrite with pyrrhotite a subordinate constituent. Pyrrhotite is absent in the sulphide-poor upper part of the reef. Bornite is present only in sulphide inclusions in chromite and substantiates and equilibration reaction involving chromite and sulphide. The high sulphide content has resulted in distinct enrichment of the Pd content over and above the normal concentration of the PGE in the UG–2 layer.

Hydrothermal activity has affected the sulphide assemblage considerably but seems to decrease in a westerly direction. In the west the effects seem to be comparatively minor and apart from dissolution of certain sulphides and the precipitation of a second generation pyrite do not seem to have affected the primary PGM assemblage.

2.7

GEOCHEMISTRY AND ORIGIN OF THE PGE MINERALIZATION IN THE MIDDLE AND UPPER GROUP CHROMITITE LAYERS AT THE LEFKOCHRYSOS MINE, SOUTH-WESTERN BUSHVELD COMPLEX

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The Lefkochrysos mine ("Lefko"), situated some 35 km west of Pretoria, is the first platinum operation in the Bushveld Complex directed at solely exploiting the PGE reserves of the UG–2 Reef. Exploration drilling has revealed major facies changes in the stratigraphy of the upper Critical Zone (uCZ) at Lefko in comparison with the Rustenburg sequence. However, the middle and upper group chromitite layers, comprising the MG–1 through MG–4 and UG–1 and UG– 2, are readily recognizable. Each chromitite layer (and associated stringers and intercalated pyroxenites) has been analysed for whole-rock Pt, Pd, Rh, Ru, Ni, Cu, Cr and Fe, together with microprobe analysis of the Cr-spinel. All of the chromitites in this package contain anomalous concentrations of the PGE's, yet base-metal sulphides (BMS's) are invariably close to background levels. The UG–2 at Lefko, which is described in detail, provides convincing evidence that the PGE's are a) fundamentally related to the chromitite; and b) were redistributed by a footwall pegmatoidal layer. Moreover, the paucity of BMS's implies partial decoupling of the PGE's and immiscible sulphide droplets during crystallization of the chromite. The Rhodes University school of thought argues that the uCZ largely developed by numerous influxes of primitive magma (preserved as cyclic units), that were injected into the chamber as hot, dense basal flows, and which "thermally eroded" the floor (dimpling, potholing and eliminating entire noritic sequences). Within the framework of this model, and in light of these new data on the chromitites at Lefko, we argue that the bulk of the PGE mineralization in the uCZ was scavenged from new influxes of magma concommitantly with the development of basal chromitite layers. Early-formed BMS's locally play a supportive role e.g., in the Merensky Reef, and postcumulus processes may redistribute the primary mineralization on the scale of a few centimetres. Finally, we interpret the uCZ of the Bushveld Complex as a unique subzone (it is absent in the Stillwater Complex), such that the Merensky and J–M Reefs are not entirely synonymous.

2.8

PLATINUM GROUP ELEMENT GEOCHEMISTRY IN THE LOWER CRITICAL ZONE IN THE WESTERN BUSHVELD COMPLEX – NEW DATA

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In the immediate vicinity of Union Section, Rustenburg Platinum Mines, where surface exposures are poor, recent drilling has provided a sequence through the lower Critical Zone. All prominent Lower and Middle Group chromitites and several minor chromite-rich layers were intersected.

Each chromitite was sampled and analysed for platinum group elements (PGE; Pt, Pd, Rh, Ru, Os, Ir) and Au using ICP mass-spectrometry; the silicate host rocks were analysed by XRF; and compositions of selected phases were determined by electron microprobe analysis.

The results show that each chromitite layer displays its own PGE signature – a general enrichment with stratigraphic height is not apparent. Inter-element ratios vary within a single layer.

Whole-rock data as well as mineral geochemistry of the silicate cumulates display compositional variations through the section resulting from an interplay between four principal features: a) major changes in modal compositions, b) systematic trends sustained through the entire sequence, c) cryptic variations recognisable through limited parts of the section and d) abrupt reversals in trends. Two major processes within the magma chamber control these variations: i) the geochemical evolution of the supernatant liquid column, and ii) the balance between crystal fractionation and repeated replenishments by a relatively more primitive magma.

The significance of these distribution patterns will be discussed.

2.9

Pt, Pd, Ir, Au AND TRACE ELEMENT GEOCHEMISTRY OF THE CRITICAL ZONE AND PORTION OF THE MAIN ZONE, RUSTENBURG PLATINUM MINE, WEST BUSHVELD COMPLEX.

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Samples of silicate cumulates of the Critical and Main Zones extending from 400 m below the Merensky Reef to 300 m above the Merensky Reef were analysed for the precious metals (PM) Pt, Pd, Ir and Au, as well as for trace and major elements.

The concentration ranges of the PM, in ppb, are: Pt, 0.62-550; Pd, 0.36-218; Ir, 0.02-18.7; Au, 0.04-58.5. The Pt/(Pt+Pd) ratio is 0.04 to 0.99. The Main Zone gabbros are depleted in PM compared with Critical Zone feldspathic pyroxenite, norites and anortosites. Highest PM concentrations (>200 ppb Pt+Pd, Ir, Au) occur in the rocks surrounding the Merensky and Bastard Reefs.

The four PM are not intercorrelated at low concentrations. There is no systematic change i the PM abundances up the sequence to the level of the Bastard Reef. Pt/Cu and Pd/Cu ratios vary greatly and are higher in the Critical Zone than on the Main Zone. Within these scattered patterns, subsets over narrow vertical intervals in the Critical Zone have depletion or enrichment trends for individual PM or for particular PM element ratios.

No correlation of Pt and Pd with Cu, Ni, or S exists. Only Ir covaries with Cr, at higher concentrations. Cu and S are not correlated at low (<50 ppm Cu, <200 ppm S) concentrations. Au and Cu correlate significantly, but not Au and S. This Au-Cu correlation suggests similar distribution coefficients on magmatic sulphide where the metals were initially concentrated; they now exist as Au-Cu alloy trapped in the cumulate, with S redistributed. Lack of PM and PM-S intercorrelation at low concentrations is evidence of late S redistribution, for those PM not controlled by primary platinum-group minerals.

2.10

FURTHER Sr-ISOTOPE AND TRACE ELEMENT STUDIES ON THE PLATREEF, BUSHVELD COMPLEX.

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Widespread reaction of Platreef intercumulus melt with floor-rock derived fluids and dolomite xenoliths has presented obstacles in determining the nature of "uncontaminated" Platreef. To address this problem, samples from an area of the Platreef inferred to be unaffected by xenoliths or proximity to granite were analysed for major and trace elements, and the Sr isotope ratios were determined.

Platreef rocks are feldspathic pyroxene cumulates which rest on a cordierite hornfels floor. The topmost gabbro and anorthosite are equivalent to the Main Zone of the Bushveld Complex. Near the contact with the gabbro there is a sequence in the pyroxene cumulates marked by a discontinuous chromitite layer, where higher PGE and base metal tenors occur.

Whole rock Mg-number defines a lower facies (Mg# 0.72 - 0.75) and an upper facies (Mg# 0.77 -0.82) for the Platreef pyroxenites and distinguishes the Main Zone (Mg# 0.67 - 0.69) from the Platreef. Trace elements (Zr, Rb, Cr, V, Y) show a geochemical break between the chromitite and the Main Zone. Whole rock Sr-isotope ratios (Ro) range from 0.7067 to 0.7087 for the Platreef. Highest Ro occurs at the chromitite, together with highest PGE tenors and highest MgO. Pyroxenites overlying the chromite have Ro of 0.7075 - 0.7076. Ro for the whole of this Platreef sequence is significantly lower than Ro previously reported for Platreef.

Trace element ratios and abundances, and the Sr-isotope data, confirm that the sulphide and the associated PGE mineralization in the Platreef are of primary magmatic origin, and are unrelated to contamination by floor rocks.

2.11

PLATINUM-GROUP ELEMENT BEHAVIOUR IN THE LOWER PART OF THE UPPER ZONE, EASTERN BUSHVELD COMPLEX – IMPLICATIONS FOR THE FORMATION OF THE MAIN MAGNETITE

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Analytical data for the six platinum-group elements and gold on 16 samples from the lower part of the upper zone and two samples from the upper part of the main zone in the eastern Bushveld Complex are presented. Almost all samples with visible sulphides contain less than 100 ppb total PGE, indicating that sulphide-enriched stratified layers in this part of the upper zone do not contain economically interesting concentrations of PGE.

Variations in PGE concentrations and Pd / Ir and Pt / Pd rations with stratigraphic height reflect differences in the compatibility of the PGE according to the sequence Ir > Rh > Ru > Pd > Pt. Rocks below and above the main magnetite layer (MML) are characterized by distinctive PGE-ratios and concentrations which are seen as the effect of an influx of a small volume of new magma at the level of the MML. This magma influx is believed to be of comparable xomposition to the large influx which occurred at the level of the pyroxenite marker in the main zone, because of similarities in the (Pt + Pd) / (Os + Ir + Ru) ratios of samples from the hanging-wall of the MML and the pyroxenite marker. Higher Os-, Ir- and Ru concentrations in the MML as well as in the magnetite enriched hanging-wall rocks compared to rocks underlying the layer, is related to an enhanced magnetite precipitation in response to a magma mixing event at elevated oxygen fugacity conditions.

PGE enrichments reported in the literature from a sulphide-bearing anorthosite below the lower magnetite layer 2 are confirmed by microscopic investigations. These are believed, on the grouds of base metal sulphide and platinum-group mineral assemblages, to represent local enrichments of possible hydrothermal origin. The chondrite normalized PGE concentration pattern of the sulphide-bearing anorthosites below the MML is similar to that of the Picket Pin Pt-Pd deposit of the Stillwater Complex which suggests similar fractionation processes in similar magma types for both complexes.

3. PGE IN KOMATIITES

3.1

PLATINUM-GROUP ELEMENTS IN THE BRAVO INTRUSION, CAPE SMITH FOLD BELT, NORTHERN QUEBEC

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The Cape Smith Fold Belt is a Proterozoic orogenic belt which lies between the Archean Churchill and Superior Provinces in northern Quebec. It contains two groups; the lower group is the Povungnituk, which consists of shelf sediments, high-Ti basalts and continental tholeiites, the upper group is the Chukotat which contains komatiitic basalts, P–MORB basalts and chemical sediments. Feeder sills and dykes to the komatiitic basalts of the Chukotat occur within the Povungnituk and Ni–Cu sulphides rich in PGE are found within them.

The Bravo intrusion is part of one of these feeder systems. The upper and lower margins are meta-picrites and the centre is a meta-poikilitic olivine cumulate. The meta-picrites contain 18–20% MgO and the incompatible trace element ratios Al_2O_3/TiO_2, Sm/Lu, Zr/Y and Ce/Yb are close to chondritic throughout the intrusion, all indicating the magma from which the intrusion formed was a komatiitic basalt. The PGE, Au, Ni and Cu contents of the rocks from the upper chill of the intrusion are similar to those found in komatiitic basalts; Os = 0.78 ppb, Ir = 0.78, Ru = 5, Rh = 1.5, Pt = 9.8, Pd = 17.8, Au = 0.71, Ni = 746 ppm, Cu =75 and the composition of the disseminated sulphides in the upper 350 m of the intrusion is similar to that found other komatiites Os = 99 ppb, Ir = 83, Ru = 489, Rh = 239, Pt = 1251, Pd = 2829, Au = 170, Ni = 9.52 %, Cu = 1.03. However, the lower 200 m of the intrusion has PGE, Au, Ni and Cu contents distinctly different from those usually associated with komatiites. There is a massive sulphide lens 1m thick in which the most extreme compositions are observed Os = 44 ppb, Ir = 109, Ru = 200, Rh = 1174, Pt = 1374, Pd = 172, Au = 4.22, Ni = 2.47%, Cu = 8.89. Disseminated sulphides in the rocks around the lens have compositions intermediate between these values and komatiitic. Sulphides of this composition cannot have formed by sulphide segregation from a komatiitic basalt, compared to komatiitic sulphides these sulphides are depleted in Pd, Au and Ni and enriched in Cu and Rh, but have similar Os, Ir and Ru contents. The sulphides are not thought to represent sedimentary sulphides because the Se/S ratios are too low 400 x 10^6. The high Cu values suggests that they might represent hydrothermal sulphides, but they do not show any enrichment of elements that might be expected in a hydrothermal system such as As, Sb, Zn (2, 0.5 and 100 ppm respectively). Further the similarity in the Os Ir and Ru contents of the sulphides with those commonly found in komatiitic sulphides suggests an alternative. Namely that the massive sulphides were komatiitic sulphides but have lost Pd, Au and Ni and gained Cu during alteration.

3.2

PLATINUM-GROUP ELEMENT DISTRIBUTION IN THE KOMATIITIC DUMONT SILL, NORTHWESTERN QUEBEC, CANADA

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The Dumont Sill is located 62 km northeast of Rouyn in northwestern Quebec. It is an Archean komatiitic intrusion emplaced into iron-rich tholeiitic volcanics of the Abitibi greenstone belt. Based on mineralogical and geochemical characteristics, Duke (1986) subdivided the sill into a mafic (MZ) and ultramafic zone (UMZ). The UMZ comprises an upper (UPZ) and a lower peridotite zone (LPZ) which consist of olivine + chromite cumulates and a dunite zone (DZ) in between them, consisting of olivine ± sulfide cumulates.

The base metal and platinum-group element (PGE) distribution has been studied on samples from 4 drill holes, which penetrate the intrusion. Three sulfide-rich layers in the DZ are delineated by anomalously high Ni, Cu, S and Se concentrations ($Ni \leq 0.95$ wt.%, $Cu \leq 0.07$ wt.%, $S \leq 1.0$ wt.%, $Se \leq 2.7$ ppm). They also contain elevated contents of noble metals ($Au \leq 20$ ppb, $Pd \leq 90$ ppb, $Pt \leq 180$ ppb, $Ir \leq 11$ ppb, $Os \leq 14$ ppb). Unmineralized samples contain <3–8 ppb Pd, 1–20 ppb Pt, 0.2–3.6 ppb Au, 0.5–6 ppb Ir, and ≤1–10 ppb Os. Thus, PGE enrichment in the sulfide-bearing zones is minimal and appears not to be of economic importance.

There appears to be a significant difference in the Ir contents of unmineralized samples from the DZ and those of LPZ and UPZ. For example, Ir concentrations in the LPZ and UPZ, which lie above and beneath the mineralized horizons have rather high Ir contents, generally between 2.9 to 4.4 ppb. In contrast, Ir contents of sulfide-free samples from the DZ and UPZ which lie immediately above the mineralized zones have significantly lower Ir concentrations, ranging from 0.1 to 1.5 ppb. Above this narrow zone of Ir depletion (5 to 10 m thick) Ir contents gradually increase up to about 6 ppb Ir. The Ir depletion is not caused by dilution effects due to the presence of interstitial liquid, because the DZ contains less than 2 % of interstitial phases. Due to the rather constant amount of chromite in the DZ, chromite fractionation is also not a likely process to have caused the Ir depletion. In fact, sulfide-free, Ir-undepleted and Cr-poor DZ samples tend to have higher Ir contents (3–6 ppb) than the Cr-rich cumulates of the LPZ and UPZ (2.9–4.4 ppb Ir). Duke (1986) observed a Ni depletion in olivine which crystallized just above sulfide-rich horizons in the DZ. It is suggested that Ir and Ni depletion in cumulates which lie between or beneath sulfide-rich zones are due to the lower Ir and Ni contents in olivine which crystallized from a silicate magma that suffered the segregation of a sulfide liquid.

Duke (1986) proposed that sulfide saturation was caused by mixing of primitive komatiite magma with fractionated interstitial liquid, which was squeezed out of the cumulate pile. Given the rather low concentrations of noble metals in the ore horizons, it appears that this process does not necessarily produce extreme PGE enrichment. Campbell and Naldrett (1979) pointed out that the relative concentrations of PGE and base metals will be a function of the R-factor, the silicate/sulfide liquid ratio. The proposed process of sulfide segregation at the floor of the magma chamber is likely a very localized event. This would imply rather low R-factors and therefore low PGE abundances in the sulfides. Thus, the small PGE-enrichment in the sulfide horizons of the Dumont Sill and the narrow zones of Ir-depletion just above the sulfide zones support the proposed process for the formation of the Ni–Cu mineralization.

3.3

PGE AND TRACE ELEMENT INDICATORS OF CONTAMINATION IN KOMATIITE-HOSTED NICKEL SULPHIDE ORES OF THE FOSTER SHOOT, KAMBALDA

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The Foster shoot, located 25 km south of Kambalda, Western Australia, is situated in a thin sequence of komatiite lavas. The lavas display textural evidence for variable rates of flow and cooling, and can be interpreted as a major linear flow channel, flanked by extensive thinner flows in a lateral facies. The ore shoot occurs at the base of and within the major flow channel, partly situated in embayment ("trough") features in the footwall, and partly on an interflow sediment layer at the contact between komatiite and footwall basalt.

Major and trace element analyses of spinifex textured komatiites at Foster reveal differences between lavas from the various flow environments. Relative to the ore-hosting flow, the flanking and overlying barren flows are both more fractionated and more enriched in levels of Zn, Zr and LREE, all elements that are abundant in the interflow sediments. The anomalous trace element compositions of the unmineralized flows can be explained by the preservation of traces of a previous sediment melting and assimilation event.

The interflow sediment layers also have relatively high sulphur contents, in the form of pyrite and pyrrhotite. Incorporation of this material into the komatiite lava might have caused sulphur saturation, and would have modified the chemistry of the subsequent sulphide liquid by dilution with iron sulphides. Analysis of mineralised samples from Foster reveal two separate ore types. Trough-associated ores have slightly lower levels of Ni and PGE in 100% sulphides + oxides, while sediment-associated ores have higher levels. In addition, the trough-associated ores have a distinct PGE pattern, with lower Os and Ir values relative to the other PGE. This would suggest that there were two separate chemical environments of ore deposition at Foster. The data are consistent with a model of contamination of a more olivine-fractionated komatiite liquid, forming the trough-associated ores, and later emplacement of an uncontaminated komatiite liquid to form flanking sediment-associated ores.

3.4

KOMATIITES AND THE MT. KEITH NICKEL DEPOSIT IN THE MT. KEITH REGION, AGNEW–WILUNA GREENSTONE BELT, WESTERN AUSTRALIA

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Three major extrusive ultramafic units are traceable over at least 60 km in the Mt. Keith region, Agnew-Wiluna greenstone belt. The stratigraphically lowest, the Eastern Ultramafic, 100–600 m thick, contains the Mt. Keith disseminated nickel deposit (270 Mt, 0.6 wt.% Ni). The overlying unit, the Central Ultramafic, 100–800 m thick, is host to basal massive sulfides at the Cliff's-Charterhall nickel deposit (2.5 Mt, 2.7 wt.% Ni). The Western Ultramafic, ~ 400 m thick, has no known associated magmatic sulfides.

The Eastern Ultramafic is predominantly a sequence of layered west-facing olivine orthocumulates. The Mt. Keith deposit occupies a large elongate zone of thickening in the sequence characterized by layered olivine adcumulates-mesocumulates, which give way progressively along strike to olivine orthocumulates with a range of proportions of interstitial liquid to cumulus olivine. At Mt. Keith, the sequence is: a basal spinifex textured flow, a zone of coarse-grained unmineralized olivine adcumulate, a thick zone of layered olivine-sulfide mesocumulates, and an upper contact zone characterized by branching, skeletal, and dendritic olivines.

The nature and distribution of igneous textures, and whole-rock major and trace element patterns (including PGM) are indicative of the Mt. Keith deposit, having formed as part of an infilled large flow channel during a period of voluminous, continuous, eruption and flow of komatiite lava.

The Central Ultramafic contains similar but smaller bodies of olivine adcumulate. In contrast however, this Ultramafic and the Western Ultramafic are predominantly sequences of thin (5–20 m) spinifex textured flows, subordinate units of olivine orthocumulate, discontinuous layered olivine cumulate-gabbro pods, and pyroxene spinifex textured flows. These ultramafic units represent flood plain sequences formed by episodic flow during the waning stages of komatiite volcanism.

3.5

THE WALTER WILLIAMS FORMATION: THE RESULT OF A REGIONALLY EXTENSIVE SINGLE KOMATIITE ERUPTIVE EVENT, YILGARN BLOCK, WESTERN AUSTRALIA

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The Walter Williams Formation is 600–800 m thick, covers > 7000 km^2 and is a major component of the central zone of the Norseman-Wiluna greenstone belt, Yilgarn Block, Western Australia. The formation is comprised of a lower zone of olivine cumulates and an upper zone of layered olivine orthocumulate-gabbro units.

In the south, the lower zone is predominantly layered coarse-grained olivine adcumulate (± chromite) but to the north there is a change to rocks with more intercumulus liquid and the development of cyclic units capped by thin layers of Mg-augite. The basal unit of the lower zone is a loosely packed olivine orthocumulate containing Mg-augite and rare oikocrysts of kaersutitic amphibole. Upwards there is a progressive change to mesocumulate and then adcumulate textures. Olivines in the adcumulate fall within the range $Fo_{87.9}$ to $Fo_{93.3}$. A thin persistent branching olivine harrisite layer occurs near the top of the lower zone. The olivine cumulates are barren of sulfide and olivine nickel (0.35–0.5 wt.% NiO) contents are indicative of sulfur undersaturation.

The upper gabbroic zone is sporadic in the south but is continuous over at least 70 km of strike in the northern half where it thickens northwards towards Kurrajong. Here, in the layered olivine orthocumulate-gabbro zone, there are two cyclic units which exhibit the sequence olivine cumulate; olivine cumulate with Mg-augite oikocrysts; diopside-olivine cumulate, diopside cumulate with plagioclase oikocrysts; diopside-plagioclase cumulate. The upper cycle has a layer of granophyric gabbro with branching harrisitic diopside above the cumulate gabbro, and is capped by a silicified flow top breccia. Geochemical profiles are indicative of fractionated komatiite liquid.

The Walter Williams Formation is believed to have crystallized during one prolonged eruptive event from the sheet flow of komatiite lava across an extensive tholeiite lava plain. The lower olivine cumulates have crystallized from the turbulently flowing lava. The upper gabbro zone has crystallized from extensive lava lakes formed during the waning stages of the eruption.

3.6

PLATINUM MINERALIZATION AT NEW NORCIA, WESTERN AUSTRALIA

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Metamorphic belts which have been affected by polyphase metamorphism about 3.2 b.y. ago occur in the Western Gneiss Terrain of the Yilgarn Block. These belts carry mafic-ultramafic remnants; one of them, Yarawindah Brook body (4 x 0.75 km), near New Norcia, W.A., has attracted particular attention as a possible source of economic PGE mineralization. Three major units of a total thickness of about 300 m constitute the Yarawindah Brook body: a) the lower mafic unit (gabbros and metagabbro-norites), b) the ultramafic unit (serpentinized meta-harzburgite to meta-dunite), c) the upper mafic unit (meta-olivine gabbronorite to meta-pyroxenites and meta-gabbro).

Primary magmatic and secondary mobilized sulphides are widespread. The former consist largely of pyrrhotite with minor pentlandite and chalcopyrite. The latter also form segregations and veins of up to 0.1 m thickness; chalcopyrite and pyrite are dominant constituents.

Hydrous silicates (chlorite, amphibole, serpentine), sulphides and PGM tend to be closely associated. Michenerite [(Pd,Pt)(Bi,Sb)Te] and testibiopalladite [Pd(Sb,Bi)Te] occur as inclusions in primary and secondary pyrrhotite, sperrylite ($PtAs_2$) and majakite (PdNiAs) are located in plagioclase, amphibole and chlorite and reach diameters of up to 0.25 mm. The mineralized zone is about 50 m thick.

Rare earth distribution patterns differ from those of differentiated intrusions by their enriched light REE. Average PGE patterns of sulphides from Yarawindah Brook resemble those of Proterozoic komatiites (Ungava, Donaldson West). The Yarawindah Brook body is interpreted as a sill-type intrusive derived from primitive mantle melts. Redistribution and concentration of sulphides and PGE to possibly economic levels has taken place during metamorphism.

4. PGE IN OTHER MAFIC-ULTRAMAFIC INTRUSIONS

4.1

DISTRIBUTION OF PGE IN SOME MINERALIZED ZONES AT THE WELLGREEN DEPOSIT, YUKON, CANADA

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Part of the Wellgreen deposit was mined as a Ni–Cu ore in 1972–73 and the deposit is currently being re-evaluated for its Ni-Cu–PGE potential. The Wellgreen deposit occurs in the Quill Creek complex, one of a number of Triassic intrusive bodies, emplaced in Permo-Triassic volcanic and sedimentary rocks of the Kluane Ranges. At present, several types of sulfide mineralization are recognized in the Wellgreen complex which consists of gabbros, peridotites and dunites.

Detailed mineralogical studies of four samples reveals differences in the mode of occurrence of the PGE and in the PGM/host mineral relationship. PGM found include sperrylite, moncheite, merenskyite, michenerite, testibiopalladite, sudburyite, kotulskite, mertieite II, stibiopalladinite, geversite, froodite and at least two unknown PGM. Electron and proton microprobe analyses show a variety of PGE-bearing minerals at concentrations ranging from a few ppm to several wt.% PGE. These minerals include melonite (Pd, Pt), breithauptite (Pd), hexatestibiopanickelite (Pd), ullmannite (Pd), pentlandite (Pd, Rh) and chalcopyrite (Rh?). Our preliminary observations suggest that a more detailed mineralogical evaluation of the PGE distribution is an important component of metallurgical test-work.

4.2

THE GEOLOGY AND GEOCHEMISTRY OF THE ROTTENSTONE NI–CU–PGE DEPOSIT, NORTHERN SASKATCHEWAN

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The Rottenstone Ni–Cu–PGE deposit is a thin Proterozoic ultramafic sill-like body that contained approximately 50,000 to 60,000 tons of ore with an average grade of 2.0 % Ni, 2.0 % Cu, 7.5 ppm Pt and 5.1 ppm Pd with significant levels of Au, Rh, Ru, Os and Ir. The deposit was intermittantly mined from 1965 to 1968 and in terms of its PGE content represents the highest mine grade of primary magmatic Ni–Cu-sulphide mineralization mined in Canada.

The intrusion is made up of an alternating sequence of net-textured harzburgites and mineralized orthopyroxenites. The associated olivines are Ni-depleted and fall in the $Fo_{83.4-85.9}$ range whereas the coexisting orthopyroxenes range from $En_{85.1-87.5}$. Chromite with up to 2.0 % ZnO and a highly variable chrome-content is also characteristic of this deposit.

The sulphur-isotope signature and S/Se of magmatic sulphide assemblages and that of the proximal country rock metasediments rules out local contamination from the known surrounding country rocks. However, geochemical studies of other similar looking sulphide-rich intrusions in the area disclosed that most are Ni and PGE-depleted and have very high S/Se ratios suggesting that significant country rock contamination of these magmas has taken place. One of the most characteristic features of the Rottenstone deposit is the presence of graphite included in sulphide. The graphite has a carbon isotope signature ($\delta^{13}C = -12.53 - 16.43$ ‰) very similar to that of graphite from the Stillwater and Bushveld Complexes.

Detailed mineralogical studies indicate that the typical sulphide assemblage is pyrrhotite, pentlandite, chalcopyrite ± cubanite. The PGM are in order of decreasing abundance: sperrylite, kotulskite and michenerite. Other metallic phases recognized are Bi-tellurides, Ag-tellurides, unnamed Co–Ni–Fe sulfarsenides and electrum. Proton-microprobe analyses reveal that pentlandite can contain between 8–17 ppm Pd, 7–20 ppm Ag and 103–139 ppm Se. Chalcopyrite was found to contain between 16 to 83 ppm Ag and 10 to 151 ppm Se.

4.3

CHARACTERISTICS OF REMOBILISED NI–CU–PGE DEPOSITS: THE D–8 AND D–9 ZONES, DELTA REGION, CAPE SMITH FOLDBELT

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In the early Proterozoic Cape Smith foldbelt (2000–1915 M.a.) two main types of Ni–Cu±PGE sulphide deposit are concentrated into two east-west trending spacialy separate zones. The sub-volcanic peridotite association found in the Raglan belt, containing the lac Cross, Katinik and Donaldson sulphide deposits and the intrusive-peridotite, differentiated sill associations found in the Expo-Ungava, Delta belt containing several small sulphide deposits. They are associated with intrusions forming part of the plumbing system to the first picritic basalts of the Chukotat Group in the axial part of the rift zone (Raglan belt) and in the rifted margins (Expo-Ungava, Delta belt).

The Delta region contains several differentiated sills and zoned ultramafic intrusions in a volcanosedimentary sequence composed mainly of high-titanium basalts and associated pyroclastics interdigitated with minor siltstones, mudstones and dolomites. The D–8 and D–9 lenses of Delta are located along an east-west trending sub-vertical shear zone cutting through three different intrusions: a peridotite dyke, a gabbroic-granophyric intrusion and a ultramafic to mafic differentiated sill. These lenses (0.05 to 10 m thickness by 50 to 150 m in length) occur over 1 km along the shear zone and contains massive sulphide breccia ore with recrystallised pyrrhotite, pentlandite and numerous fragments of enclosing rocks, partially digested and rimmed by chacopyrite, especially abundant in the upper half of the ore. There is mineral layering and contacts with enclosing rocks are sharp and often sheared.

The D–8 lens has average Ni, Cu and PGE contents of respectively Ni = 6.65%, Cu = 0.985%, Ir = 71.1 ppb, Os = 43.9 ppb, Ru = 389.6 ppb, Rh = 433.9 ppb, Pt = 1112.9 ppb, Pd = 756.0 ppb and Au = 42.7 ppb on an 9.6 meters intersection and the D–9 lens has average contents of Ni = 5.17%, Cu = 1.4%, Ir = 16.8 ppb, Os = 17.0 ppb, Ru = 41.3 ppb, Rh = 219.4 ppb, Pt = 1768.0 ppb, Pd = 2768.0 ppb and Au = 24.8 ppb on a 5.4 meters intersection. Merenskyite, sudburyite, kotulskite, sperrylite and testiobiopalladinite have been identified as small inclusions in pyrrhotite, pentlandite and chalcopyrite, in the massive sulphide lenses and in the surrounding veins. Both lenses exhibit the same general characteristics except for a difference in their PGE ratios. They show a vertical zonation, the base being richer in Ir group elements (base: D–9, Pd/Ir=23; D–8, Pd/Ir=15.5) becoming richer in Pd group elements and poorer in Ir group elements as we go up in the stratigraphy of the ore (summit: D–9, Pd/Ir=5865.0; D–8, Pd/Ir=81.25).

These sulphide lenses are thought to represent original magmatic sulphide segregation later remobilised during a tectonic event. A late hydrothermal event is also present as witnessed by stringer-type Cu–Ni–PGE mineralisation surrounding the massive sulphide lenses. Magmatic versus post-magmatic mechanisms for the geochemical differences in the lenses will be discussed.

4.4

PLATINUM GROUP MINERALS FROM THE TWO DUCK LAKE INTRUSION, COLDWELL COMPLEX, CANADA

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The Coldwell alkaline complex located on the north shore of Lake Superior is a composite Proterozoic intrusion. The platinum group elements (Pt/Pt+Pd = 0.2) associated with a Cu-rich (Cu/Cu+Ni = 0.9) sulphide deposit occur within a coarse grained to pegmatitic gabbro-monzonite of the Two Duck Lake intrusion in the eastern margin of the Eastern gabbro. The base metal sulphides (BMS) include pyrrhotite, pentlandite, argentian pentlandite lamellar intergrowths of chalcopyrite with cubanite, pyrite, bornite converted to neodigenite and covellite. Pyrrhotite is generally Ni enriched (up to 0.4 wt.%) whereas pentlandite is highly enriched in Co (up to 3.4 wt.%). The sulphides are mainly interstitial in association with Cl-rich (up to 0.6 wt%) intercumulus hydrous silicates (amphibole, biotite) and fluorapatite also enriched in Cl (up to 0.6 wt.%). The associated oxides are ilmenite and titanomagnetite. The PGM occur in Cu-rich sulphides. Temagamite (Pd_3HgTe) is commonly rimmed or replaced by kotulskite (PdTe) or surrounded by altaite (AgTe). Merenskyite (Pd_2Te), isomertierite ($Pd_{11}Sb_2As_2$), mertierite II (Pd_8Sb_3), atokite (Pd_3Sn) and zvyagintsevite (Pd_3Pb) are the other Pd rich minerals. The arsenides and sulpharsenides are represented by sperrylite ($PtAs_2$) and hollingworthite (RhAsS). Hollingworthite is highly zoned, the core being rich in Ir whereas the outer zone is enriched in Os and Rh. The As/S ratio also varied during growth, indicating an increase of sulphur fugacity in the metasomatic fluids. The final stages were characterized by the appearance of electrum (Au, Ag) and clausthalite (PbSe).

4.5

MAGMATIC CONTROLS ON THE PLATINUM GROUP ELEMENTS IN VOLCANIC AND PLUTONIC ROCKS OF THE CAPE SMITH BELT (NEW QUEBEC, CANADA)

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PGE contents in igneous rocks of the early Proterozoic Cape Smith Belt depend on the nature of the parental magmas. This region contains two tectono-stratigraphic domains separated by a major east-west thrust fault, each representing the opening of separate oceanic basins. In the southern domain, the low MgO and LREE-enriched tholeiitic basalts (MgO = 3–9%) of the Povungnituk Group possess low PGE contents (<10 ppb), and their comagmatic gabbroic sills contain no PGEs. The high-MgO komatiitic olivine-phyric basalts (MgO = 19–11%) of the Chukotat Group contain relatively high PGE contents (25–35 ppb), whereas more differenciated tholeiitic pyroxene-phyric (MgO = 12.5–7%) and plagioclase-phyric basalts (MgO<8%) contain lower PGE contents (17 to 30 ppb and <10ppb respectively). This correlation between MgO and PGE contents is confirmed by chilled margin compositions of comagmatic ultramafic and mafic intrusions, demonstrating that the more magnesian the parental liquid, the higher the PGE content. Thus, the peridotitic and pyroxenitic intrusions, which correspond to the less fractionated komatiitic parental liquids (MgO = 23–18%), have the highest PGE contents (ΣPGE=90–35 ppb). They also contain magmatic Ni–Cu–PGE deposits, demonstrating that sulfur saturation occurs early in the magmatic evolution, also explaining the low PGE contents of the more evolved liquids. Indeed, parental liquids of the peridotitic to gabbroic differentiated sills (MgO = 19–15%) are depleted in PGEs (19–10ppb) and sulphide mineralization is rare, except in some upper gabbroic units (Delta 3 sill) where PGE mineralization occurs locally in a "reef".

The northern domain contains one of the oldest ophiolite suite (1999 Ma, St-Onge et al., 1987, 1988; St-Onge and Lucas, 1989; Scott et al., 1988), demonstrating the formation of a Proterozoic oceanic crust. The plutonic rocks exhibit various PGE/chondrite profiles from enriched IPGE (Os–Ir–Ru) profiles in chromitic levels to depleted IPGE profiles in peridotitic to gabbroic cumulates. They have relatively high PGE contents (ΣPGE = 90–15ppb), whereas the derived low-MgO and LREE-depleted tholeiitic basalts (MgO = 11–5%) have lower PGE contents (ΣPGE = 15–5 ppb). PGE concentrations occur in chromite-rich peridotitic layers (ΣPGE = 100–635 ppb) and locally in small Cu deposits (ΣPGE = 60–100 ppb)associated with thrust faults.

Thus, the PGE contents in plutonic rocks appear to depend on the degree of fractionation and MgO contents of parental liquids, on the timing of sulfur saturation, and on the sulfur or oxygen fugacity in the magmatic system. Progressive partial melting, displayed by the genesis of Chukotat basalts, probably influenced the observed PGE behaviour in magmatic liquids.

4.6

CONTRASTING PGE PROFILES IN CHROMITITE FROM THE FINERO ULTRAMAFIC COMPLEX, IVREA ZONE, ITALY

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The Ivrea zone consists of continental crust made up of amphibolitic to granulitic metasediments and metavolcanics intruded by a mafic/ultramafic complex which is divided into 5 parts; the peridotite massifs of Balmuccia, Baldissero and Finero; the Cyclic Units consisting of a layered series of peridotites, pyroxenites and gabbros; the Main Gabbro; the ultramafic sill of La Balma-Monte Capio; and a series of Ultramafic Pipes.

The Finero complex forms an antiformal structure, cropping out as a concentrically zoned ellipsoid 12 x 2 km, emplaced into amphibolite facies rocks. Four lithostratigraphic units are distinguished outwards from the centre; the phlogopite peridotite, the lower gabbro, the amphibole peridotite and the upper gabbro. Unpublished exploration data and recent field work have revealed the presence of chromitite bands at several localities in the marginal zone of the phlogopite peridotite.

Three possibly separate horizons have been identified in one area and have proved to have very different PGE profiles. The two samples from horizon 1 have chondrite normalized (C_n) abundances for Ir, Os and Ru of about 0.1 to 0.2, for Rh of 0.05–0.08, for Pt of less than 0.01, and Pd abundances below detection but lower than Pt. Six samples from horizon 2 have low Ir (C_n abundances of from 0.004 to 0.014), Rh between 0.14 and 0.45, and, Pt values below 0.01. The one sample obtained from horizon 3 has Cn abundances for Os, Ir, Ru and Rh all between 0.25 and 0.38, and a very much higher abundance of Pd (nearly 0.1) than the other samples. Most samples from other areas of the phlogopite peridotite show the high Rh and low Ir characteristic of horizon 2.

The contrast between the PGE abundances of horizons 1 and 2 can be explained as the result of fractional crystallization of olivine during formation of the phlogopite peridotite, although this is inconsistent with Rivalenti et al's (1981) interpretation of the complex as metasomatised depleted mantle. The higher Pd content of horizon 3 can be due to the presence of original sulfide.

4.7

PGE IN MAGMATIC SULFIDES FROM THE IVREA ZONE: THEIR CONTROL BY SULFIDE ASSIMILATION AND SILICATE FRACTIONATION

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Small-sized deposits of Ni–Cu sulfides with associated platinum-group minerals are found in all units of the mafic/ultramafic complex of the Ivrea Zone (see Ferrario et al, this volume), with the exception of the mantle fragments.

Distinctive ore types are associated with different units. In the Layered Series ore mostly occurs in pyroxenite layers close to or in contact with metasediments. In the Main Gabbro, the ore is associated with pyroxenite layers close to the base. In the La Balma-Monte Capio sill, ore occurs close to the base in contact with metasediments, and also well inside the ultramafic sequence. In the ultramafic pipes, nodular aggregates of sulfide typically associated with hydrous silicate minerals are the most common type of mineralization.

Deposits in the Layered Series have low overall concentrations of the PGE (Pt_{CN} 0.05; Ir_{CN} 0.005), low Ni and Cu (1–2 and 0.1–0.5 wt.% respectively in massive sulfides), and low Ni/Co ratios close to or below 10. The average $(Rh/Ir)_{CN}$=6.5, and $(Os/Ir)_{CN}$=2.2. The PGE concentrations in the Sella Bassa deposit in the Main Gabbro are approximately an order of magnitude higher than in the Layered Series. $(Os/Ir)_{CN}$ ratios range from 0.48 to 0.65 in contrast to ratios of 2 or more found elsewhere. Also the Pd/Pt ratio and Ni content of sulfides (3.5–4.5 wt%) is much higher. PGE profiles of deposits within the La Balma-Monte Capio intrusion resemble those of the Layered Series, although both Ir and Os trends are distinctly higher, resulting in an average $(Rh/Ir)_{CN}$ ratio of about 2.9 instead of 6.5, and Ni and Cu are also distinctly higher. Deposits at the base of the intrusion have generally very low Ni, Cu and Co in addition to low PGE. The richer pipes have considerably higher Os, Ir and Ru (0.15 x chondritic abundance) than all other deposits from the Ivrea Zone, and Pt and Pd concentrations of the order of those at Sella Bassa.

The low PGE values of the deposits of the cyclic units are attributed to these having experienced a low R value (magma/sulfide ratio) during their segregation. Contrasts between the La Balma-Monte Capio deposit and those of the layered series are attributed to variable fractionation of a similar magma. The Main Gabbro hosting the Sella Bassa deposit appears to have been deficient in PGE, and to represent a different magma.

4.8

NOBLE METALS SEGREGATION AND FRACTIONATION IN MAGMATIC ORES FROM RONDA AND BENI BOUSERA LHERZOLITE MASSIFS (SPAIN, MOROCCO)

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The lherzolite massifs of Southern Spain and Northern Morocco are high-temperature mantle intrusions emplaced into continental crust. Three types of mineralization are found : (Cr) chromite, (Cr–Ni) chromite–nickel arsenide, (S–G) sulphide–graphite. The ore veins are distributed in this order from the plagioclase-lherzolite core to the garnet-lherzolite border of the massifs. These high-temperature ore assemblages (1200–600°C) have cumulate textures including orthopyroxene and/or cordierite as their main silicate minerals.

High average PGE values are found in the Cr–Ni ores (2900 ppb PGE) in relation with the Ni-arsenide abundance ; the Cr ores have only 1050 ppb PGE and the S–G ores are PGE-poor (350 ppb), gold follows the PGE distribution : 13 000 ppb in Cr–Ni ores , 570 ppb in Cr ores, and only 93 ppb in S–G ores. The chondrite normalized PGE patterns of the Cr–Ni ores are flat and chondritic, whereas those of the Cr and S–G ores have respectively a negative and a positive slope. The Pd/Ir ratio strongly increases from the Cr ores (0.65) to the Cr–Ni and the S–G ores (4. and 6.1). There are some $(Os, Ru)S_2$ inclusions in the chromite of the Cr ores. In the Cr–Ni ores, some minute Au, Au–Cu, and Au–Bi–Te grains are observed ; but no PGM have been found, except in a weathered Cr–Ni ore where abundant PGM ($PtAs_2$, IrAsS) have been discovered, suggesting that PGE may be hidden in solid solution in the Ni-arsenide.

The ore-forming magma was probably generated from a mantle source-rock. The earlier chromites (Cr ores) included Os–Ir–Ru minerals, whereas most of the gold and remaining PGE with higher Pd/Ir ratio were partitioned into an immiscible As–S–liquid which fractionated later in a PGE–Au–rich NiAs-phase (Cr–Ni ores) and then in a PGE–Au-poor MSS-phase (S–G ores).

4.9

GEOCHEMICAL STUDY OF PGE AND Au IN CHROMITITES AND PYROXENITES OF PRECAMBRIAN ULTRAMAFIC INTRUSIVE BODIES, CENTRAL NORTH MADAGASCAR

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The granulite facies Archaean rocks in the Andriamena area of north central Madagascar are intruded by small ultramafic-mafic bodies, up to 0.5 x 1.5 km, of dunite, pyroxenite and gabbro. Two types of mineralization are present in these intrusions, chromitite, in places as large bodies, and disseminated base metal sulphides (BMS) with local concentrations.

Thirteen samples, comprising massive and disseminated chromitite, ranging from 13 to 46% Cr_2O_3, and pyroxenite were analysed for all the platinum-group elements (PGE) and for Au. High contents of Os, Ir and Ru have been determined for the chromitites, whereas the pyroxenites, although rich in Pt and Pd, contain very little Os, Ir and Ru.

Two types of (chondrite normalized) PGE distribution can be distinguished among the chromitites:

1. "Ophiolitic", with strong Os, Ir and Ru enrichment.
2. A distribution marked by high contents of Rh, Pt and Pd associated with high contents of Os, Ir and Ru regardless of Cr_2O_3 values.

In both types of distribution, the high Os, Ir and Ru values are due to the presence of platinum-group minerals (PGM), Os–Ir alloys laurite, as inclusions in chromite. The enrichment in Rh, Pt and Pd, on the other hand, appears to be related to either the presence of the PGM (sperrylite) associated with base metal sulphides, or to the PGM directly enclosed in the chromite. Similarly, in the pyroxenites rich in PGE, PGM (sperrylite, moncheite, arsenopalladinite and electrum) may or may not be associated with the BMS. The PGE concentration is thus unrelated to the amount of BMS mineralization, but is in all cases directly determinated by the nature of the PGM.

4.10

MINERALOGY OF PGE IN MAFIC-ULTRAMAFIC MASSIFS OF THE KOLA REGION

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Over the last years more than 10 previously unknown PGE minerals have been identified in the nickel-bearing mafic-ultramafic massives: palladium, melonite, merenskyite, moncheite, michenerite, kotulskite, sobolevskite, sperrylite, vysotskite, braggite, sopcheite, cooperite, palladium, gold and a mineral of $Pt_2(Fe,Bi)_3$ composition. The peculiarities of PGE mineralization in various massives and its formation under magmatic and hydrothermal conditions are established. A wide manifestation of isomorphism was recognized in some series of minerals. The PGE mineralization of the region features predominance of bismuthotellurides of palladium and platinum over sulphides, most of the PGE being part of monosulphides and sulpharsenides of iron, nickel and cobalt.

4.11

PLATINUM-GROUP ELEMENT MINERALIZATION IN THE MECHANIC INTRUSION OF THE APPALACHIAN OROGEN

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The Mechanic intrusion is one of the numerous tholeiitic mafic-ultramafic intrusions occurring in the Appalachian Orogen. The lenticular intrusion is layered and consists of peridotite, troctolite, olivine gabbro, olivine gabbronorite, gabbronorite, pyroxenite, anorthosite and gabbro. Field studies revealed the existence of at least three major cyclic units, each beginning with peridotite. Platinum-group element mineralization discovered following detailed mapping of the intrusion occurs in two zones. Zone I characterized by the presence of interstitial sulfides up to 5 % occurs in the feldspathic peridotite of the lowermost cyclic unit. Typical Os, Ir, Ru, Rh, Pt, and Pd concentrations of this zone are 15, 12, 23, 43, 480, and 1600 ppb respectively. Zone II occurs in the olivine gabbronorite of the uppermost cyclic unit. Coarse grained blebby sulfides forming up to 8% of the rock are associated with the pegmatitic portions rich in hydrous phases. Combined PGE concentration of this zone is 2600 ppb. Platinum-group minerals identified to date are vysotskite, merenskyite, michenerite, sperrylite, stillwaterite and hollingworthite. Electrum and native gold are the other precious metal-bearing minerals. Chondrite-normalized plot of PGE concentrations in the sulfide fraction display similar patterns to those of flood basalt related ores.

4.12

PLATINUM-GROUP MINERAL ASSOCIATION IN CHROMITITES OF THE KIMPERSAI ULTRAMAFIC MASSIF

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A diverse association of platinum-group minerals has been found in massive and densely-impregnated chromitites of the Kimpersai ultramafic massif (the Southern Urals). Besides hexagonal and cubic solid solutions of the system Os–Ir–Ru and sulfides of the series of laurite-erlichmanite common to chromitites, there occur compounds of iridium, osmium and ruthenium of various natural classes, as well as several nickel minerals containing platinum metals in the solid solution.

Minerals of the system Os–Ir–Ru are represented by ruthenium-poor phases forming the series $Os_{0.8}Ir_{0.1}Pt_{0.06}Ru_{0.02} - Ir_{0.62}Os_{0.38}$. Metallic solid solutions of this system are in equilibrium with minerals of the laurite-erlichmanite series. Two-mineral aggregates, in which ruthenium-rich but osmium- and iridium-poor sulfide coexists with ruthenium-poor but iridium- and osmium-rich metallic solid solutions commonly occur.

Within the group of metallic solid solutions of great interest are "porous alloys" represented by minerals of the system Ir–Os–Fe–Ni and by phases of Cu–Os system unknown in the nature. Amounts of the main components in the minerals of the system Ir–Os–Fe–Ni vary greatly up to the binary compounds Ir–Ni, Ir–Fe, Ru–Fe, Ru–Ni and $Ru–Fe_2$. Phases $Os–Cu_2$ and Os–Cu have been revealed in the Cu–Os system. The group of "porous alloys" is associated with $Ru–As_2$, ruarsenite, irarsite and ruarsite. The latter are common in growths rich in iridium (up to 10% of the mass) and osmium (up to 2% of the mass) and maucherite.

Platinum-group minerals from chromitites of the Kimpersai massif refer to the two parageneses. The first

– including ternary alloys and Ir,Os,Ru sulfides represents an early paragenesis syngenetic to chromitite formation. The second – consisting of "porous alloys", sulfoarsenides and arsenides, developes as a result of the metamorphic transformation of minerals of primary paragenesis.

4.13

NOBLE METAL MINERALIZATION AND ITS POSITION IN THE PROCESS OF THE Cu–Ni SULFIDE ORE FORMATION

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The detailed study of the Platinum-Group Minerals (PGM) from the different types of the Cu–Ni ores shows that the principal part of the platinum mineralization is connected with the process of the subsolidus transformation of the main ore forming sulfides. The PGM with the greatest diversity of their composition are generally occurred in the Cu-rich sulfide ores composed mainly of the chalcopyrite-group minerals (talnakhite, mooihoekite, putoranite), cubanite, and bornite. Many Platinum-Group Element partners (Sn, Pb, Bi, As etc.) took part in the final stage of the ore formation.

The PGM are assoiciated with the rare ore minerals (shadlunite, djerfisherite, thalcusite, valleriite) and with minerals unusual for the Cu-Ni sulfide ores (sphalerite, galena, clausthalite, altaite etc.). The study of these minerals permits to limit the temperature range by 450–200°C for these associations. The PGM compositions is connected to the temperature decreasing. The sequence of PGM is in general: stannides– arsenides; tinarsenides and/or tin-antimonides, arsen-antimonides; cooper-stannides; compounds with lead, lead and sulfur; compounds with bismuth and bismutho-tellurides.

There are two possible sources of PGE forming PGM: 1) the solid solutions in the main ore sulfides, 2) the residual magmatic fluids – the product of the magmatic differentiation. These fluids included along with PGE and volatile components such elements as Pb, Te, Bi, Tl etc. It is possible also that the part of these elements was brought by hydrothermal solutions during the postmagmatic ore transformation.

There is no simple solution of the PGE-transport problem. The most widespread opinion about the chlorine nature of the fluids is confirmed by the fluid inclusion study of the PGE-bearing rocks (C. Ballhaus, E. Stumpfl). The PGE-transport and PGM-recrystallisation was proved by the experimental study of the systems Pd–Cu–Sn–(HCl), Pt–Fe–S–O–(HCl), Pt–Cu–Pb–S–(HCl) etc. The experimental conditions (1–5 wt.% Cl, $P=10^{-8}$ Pa, $t°=300–400°C$, $\lg fO_2= -35$ Pa) are comparable with the natural observations and are in good agreement with the genetic model of the sulfide liquid differentiation when the sulfides crystallize and PGE, Pb, Bi, Te are accumulated in the residual fluids.

4.14

ASSOCIATIONS OF PLATINUM-GROUP MINERALS IN VEINLET-DISSEMINATED COPPER-NICKEL ORES OF THE TALNAKH ORE DEPOSIT

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Thirty platinum-group minerals (PGM) have been found in veinlet-disseminated ores in metamorphic and metasomatic rocks of the exocontact and partially of the endocontact of ore-bearing intrusives. These ores form zonal bodies around massive ores with a different mineral composition of individual zones.

Each ore variety is characterized by a specific set of PGM. Chalcopyrite-pyrrhotite and pyrrhotite-chalcopyrite ores forming the inner part of ore bodies contain isoferroplatinum, sperrylite, arsenides, arsenostannides and stibioarsenides of palladium and nickel. Isoferroplatinum forms mirmecite intergrowts with monoclinic pyrrhotite ($Fe_{0.83}S$ – $Fe_{0.86}S$). The other PGM form intergrowths such as: $Pd_2(Sn,As)$ + $(Pd,Ni)_2(As,Sb)$ and sperrylite + Pd_5As_2 + palladoarsenide + $(Pd,Ni)_2As$.

In pentlandite-chalcopyrite, millerite-pentlandite-chalcopyrite and millerite-chalcopyrite ores PGM are represented by kotulskite, michenerite, moncheite, vysotskite, sopcheite and sperrylite. They form intergrowths and single grains.

Millerite-bornite-chalcopyrite ores contain telargpalite, kotulskite, (Pd,Pt) (Pb,Bi) (S,Se), $(Pd,Ag)_3$ (Ag,Pb) (Te,Se), tulameenite and vysotskite. Tellurides, bismuthotellurides, selenotellurides and selenosulfides form intergrowths. Vysotskite is often a single representative of PGM in these ores. The occurrences of the copper-lead-platinum sulfides such as kharaelakhite, are characteristic of these ores.

Chalcopyrite ores with pyrite and millerite forming external zone of ore bodies contain platinum, palladium and silver sulfides. Cooperite, braggite and vysotskite form single grains but also occur in intergrowths with other PGM such as cooperite + braggite + telargpalite + sopcheite + mertilite + $(Ag,Pd)_3S$ + $Pd_5Bi_3S_3$.

In veinlet-disseminated ores developed around chalcopyrite, talnakhite, mooihoekite and culbanite massive ores, PGM are represented by palladium and platinum intermetallides (polarite, stannopalladinite, taimyrite, palladium rustenburgite, platinum atokite, $Pd_2(Sn,As)$, mayakite, $Pd_3(As,Sb,Sn)$, sobolevskite, kotulskite, tetraferroplatinum and sperrylite. Minerals mainly form intergrowths.

4.15

THE KEY WEST MINE: PROTEROZOIC, MAGMATIC/ HYDROTHERMAL Ni-Cu-PGE DEPOSIT IN NEVADA

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The Key West deposit is located within an erosional window of Proterozoic metamorphic rocks near Lake Mead, 70 miles northeast of Las Vegas, Nevada. Mineralization is confined to a tabular, inclined mass of amphibolitized ultramafic rock which is embedded on multiply-deformed granodioritic orthogneiss. The ore-bearing intrusion is one of a series of small ultramafic and mafic bodies distributed in trains or as individual masses within a narrow, linear zone broadly conformable with regional foliation.

Primary rock textures and mineralogy are masked by the effects of upper amphibolite facies metamorphism, poly-phase folding and intense, near-surface oxidation. Relict igneous silicate assemblages and whole-rock data indicate that protoliths included peridotite, harzburgite, websterite, and clinopyroxenite.

Cu-Ni-PGE sulfide mineralization occurs as disseminations interstitial to silicates, and less commonly as semi-massive matrix or breccia ore. Although ultramafic rocks are the most important ore host, significant mineralization is hosted by crosscutting quartz-plagioclase-microcline pegmatites and wall rock gneiss. Pyrite and chalcopyrite are the dominant sulfides with subordinate pentlandite, pyrrhotite, secondary Cu-Ni phases and Pt-Pd tellurides. Overall, Cu:Ni and Pt:Pd approach a constant value of 1.5:1.

The importance of both ultramafic rocks and late, felsic pegmatite as hosts to mineralezation suggests a complex genesis in which precursor magmatic sulfides were remobilized by hydrothermal processes. The Key West deposit should probably be classed as a Shear-Zone-Related hydrothermal deposit, as defined by McDonald (1987), although there are strong affinites with the magmatic deposits of Allarechka and Lovnoozero camps, Kola Penninsula, U.S.S.R.

REFERENCE: *McDonald, A.J.*, 1987; Geoscience Canada, V. 14, #3, p. 155 - 166.

5. PGE IN OPHIOLITES

5.1

NOBLE METALS IN COBALT-ARSENIDE ORES: HYDROTHERMAL CONCENTRATION FROM A SERPENTINITE SOURCE-ROCK (BOU AZZER, MOROCCO)

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The cobalt-arsenide ores of Bou Azzer are located along the borders of serpentinite massifs (Upper Proterozoic ophiolite) in carbonate-quartz lenses resulting from an hydrothermal carbonate alteration of serpentinite that is assumed to be the source-rock of cobalt. The cobalt ores contain an average gold content of 5–15 ppm; gold is mainly located in skutterudite (20–400 ppm) whereas Fe-arsenide (loellingite) contains only 1–2 ppm Au. Preliminary investigations on the PGE distribution show that platinum is erratically distributed in the cobalt ores (20–2500 ppb), the higher values are found in skutterudite and the lower in loellingite. The Pt/Pd ratios is also high in skutterudite (> 3) and low in loellingite (≤1). The chondrite normalized PGE patterns of the arsenide ores are W shaped with relatively low Ir an Rh, and high Ru values, resembling thus to the PGE pattern of some magmatic sulphide ores except for the low Pd content of the skutterudite ores. In serpentinite the PGE patterns are flat and the Pt values are ≤ 6 ppb in the same range that gold values (3–5 ppb) ; but the corresponding accessory opaque minerals display distinct characteristics :

	Pt(ppb)	Pt/Pd	Au(ppb)	PGE pattern
Magnetite	7–21	< 1	10	W shaped
Chromite	10–70	> 1	7	steep negative slope
Sulfides	80–800	> 8	15	strong Pt positive anomaly

During serpentinization PGE and gold were concentrated in secondary sulphides and magnetite. During late hydrothermal carbonate alteration, these minerals were then destroyed and gold, and at a lesser extent platinum, were preferencially transported in arsenic-rich fluids and precitated with the skutterudite, probably in solid solution.

5.2

GEOCHEMISTRY AND MINERALOGY OF PLATINUM GROUP ELEMENTS IN CHROMITITES FROM TROODOS, CYPRUS

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We present the results of a comprehensive investigation of the distribution of platinum group elements and minerals in the Troodos ultramafics. Reflected light microscopy, electron probe microanalysis and neutron activation analysis have been the main methods used. A variety of platinum group minerals, comprising sulphides and alloys, has been identified in chromitites from Troodos. These are up to 30 μm in size and generally occur as inclusions within chromite but have also been detected in the serpentinized matrix of chromitites. PGM frequently have an attached silicate phase (clinopyroxene, serpentine and, more rarely, phlogopite). Laurite (RuS_2) with variable amounts of Os and Ir is the most abundant phase. Other sulphides include cooperite (PtS) in association with laurite, Rh–Ir-bearing Ni–Fe–Cu sulphide, and a Pt–Ir sulphide associated with the Rh–Ir-rich phase. Alloys comprise iridosmine (Os, Ir), osmian ruthenium (Ru, Os) and two Fe-rich phases (Ru, Fe) and (Ir, Ru, Fe). With the exception of iridosmine, these alloys are related to cracks and alteration and their genesis is ascribed to the reduction of laurite. Further evidence for former strongly reducing conditions is provided by the existence of abundant awaruite (Ni_3Fe) in the matrix of chromitites. This is the first time most of these phases have been reported from Troodos although a similar assemblage has been observed in Oregon ophiolites (Stockman and Hlava, 1984). The euhedral nature and apparently random distribution of PGM is compatible with mechanical entrapment within crystallizing chromite. The widespread occurrence of laurite indicates a moderately high, though variable activity of sulphur in the melt, although the existence of iridosmine implies locally lower activities. The secondary alloys formed by later desulphurization and, occasionally, introduction of Fe. There is increasing evidence for low-temperature secondary redistribution of PGE in ophiolites linked to serpentinization. This study shows that similar remobilization has also occurred in the Troodos chromitites.

5.3

SILICATE, SULPHIDE AND PLATINUM MINERAL INCLUSIONS IN CHROMITES FROM THE EASTERN ALPS, AUSTRIA

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Two major ultramafic massifs, Kraubath (13 x 2 km) and Hochgrössen (2 x 2 km), occur near the northern rim of the Central Alps in Styria, Austria. They represent rootless dismembered parts of an early Paleozoic ophiolite. Chromitites as layers and schlieren occur in both massifs. Extensive reflected light and microprobe studies have revealed the presence, in chromitites, of a vast spectrum of solid inclusions of silicate and platinum group minerals. These occur exclusively within the core zones of homogeneous, primary chromites, and comprise olivine, orthopyroxene and amphibole. Olivine (30 – 120 μm) is Mg-rich (Fo_{98}) and carries 0.1 to 0.3 % Ni, orthopyroxene is En_{90}, and amphiboles are alkali-rich with up to 2.1 % Na_2O. Ferritchromite rims also carry phyllosilicates. Chlorites are Mg-rich with up to 3.8 % Cr_2O_3; there are no compositional differences between inclusion chlorites and matrix chlorites. The same applies to serpentine, which carries up to 2.4 % Cr_2O_3, and, in the vicinity of sulphides and/or PGM, up to 0.6 % Cl.

Two types of sulphide inclusions have been identified: a) pentlandite, chalcopyrite and heazlewoodite in chromite cores, b) pyrite, arsenopyrite and galena in altered chromite rims, While the former are considered coeval or earlier than chromite, the latter are products of serpentinization and metamorphism.

Platinum group minerals include sulphides, sulpharsenides, arsenides and alloys. Cooperite (PtS), laurite (RuS_2), members of the ternary RhAsS–IrAsS–PtAsS system, sperrylite and alloys of platinum with minor Os, Ir, Rh and Pd, as well as Pd–Sb–Pt alloys have been identified. Analytical evidence reveals enrichment of Ir, Os, Ru (IPGE) versus Pt, Pd and Rh (PPGE) in the investigated chromitites, and this agrees well with the preponderance of IPGE-rich primary PGM inclusions, and with data from ophiolites world-wide. On the other hand, high PPGE abundances at Hochgrössen are an expression of widespread Rh–Pt–Pd sulpharsenides. This points towards significant redistribution of PGE during serpentinization and metamorphism.

5.4

MAGMATIC FRACTINATION OF PGE IN THE SHETLAND OPHIOLITE COMPLEX

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The Shetland ophiolite complex exhibits the lower part of the classic Penrose ophiolite sequence (Prichard, 1985). Concentrations of chromite in the dunite unit and in dunite lens wihtin harzburgite show ophiolitic compositions, and the dyke geochemistry indicates and supra subduction zone origin for the complex (Prichard and Lord, 1988).

PGM containing all six PGE have been found in chromite-rich lithologies from the complex. PGE analysis showed that chromite-rich samples from within a dunite lens at Cliff give positive slopes on a chondrite normalised PGE diagram similar to those found in stratiform complexes. Chromite-rich samples from elsewhere in the complex give negative slope patterns typical of other ophiolites (Prichrad *et al.*, 1986).

This paper examines the pattern of PGE concentration throughout the complex. Positive slope PGE patterns are widespread, occurring in dunites and disseminated chromite-rich dunites from both mantle and crustal sequences, wehrlites and pyroxenites. The PGE are enriched in lithologies containing accessory Ni-Cu sulphides. The distribution of PGE, Ni and Cu in the complex all show primary lithological associations, indicating a magmatic origin. PGE enrichments occur at the base of magmatic cycles.

Comparison of the chondrite normalised patterns at different stratigraphic levels indicates fractionation of the six PGE. Os, Ir, Ru dominant negative slope patterns occur exclusively at low stratigraphic levels in chromite-rich rocks. Pt, Pd, Rh dominant positive slope patterns occur at higher levels, and are steeper in pyroxene bearing lithologies.

Negative Pd anomalies in samples from shear zones suggests higher mobility of this element.

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5.5

PGE-GEOCHEMISTRY OF BONINITIC AND BASALTIC ROCKS OF THE KARMØY OPHIOLITE COMPLEX, WESTERN NORWAY

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The Karmøy ophiolite formed by polyphasal magmatism and the complex exhibits rocks of MORB-like, IAT-like, boninitic, calc-alkaline and alkaline affinity. The various magma series of the complex show a negative correlation between the heavy rare-earth elements (HREE) and the PGEs, were the PGE concentrations increase exponentially with decreasing HREE concentrations of the rocks. Lithophile trace elements and Nd isotope systematics suggest that the progressive decrease in HREE is due to an increasing degree of partial melting of a depleted mantle source.

Boninitic dykes represent the most PGE-enriched magmas of the complex with total PGE concentrations of ca. 20 ppb, nearly ten times higher than that of the MORB-like rocks. The complex also exhibits, however, a suite of PGE-depleted boninitic dykes. The presence of Ni-sulfide mineralized boninitic dykes as well as a massive, PGE-rich (8 ppm total PGEs), Cu-Ni sulfide deposit suggests that the bimodal PGE concentrations of the boninites reflect sulfur saturation. This is supported by the fact that the PGE- enriched and the PGE-depleted boninitic rocks have similar Os and Ir concentrations while they differ markedly in the chalcophile PGEs such as Pt and Pd. The PGE-depleted boninitic rocks and the MORB- like rocks exhibit comparable chondrite normalized PGE-patterns. They differ, however, in that the MORB-like rocks exhibit a marked negative Ru-anomaly which is not seen in the boninitic rocks. This feature may reflect contrasting degrees of fractionation in crustal magma-chambers.

5.6

MAGMATIC AND SECONDARY PGM IN THE SHETLAND OPHIOLITE COMPLEX

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Unusually enriched PGE concentrations in the Shetland ophiolite complex are associated with a great variety of PGM not traditionally thought to occur in ophiolite complexes (Pichard and Tarkian, 1988; Tarkian and Prichard, 1987). Initial studies involved chromite-rich lithologies in dunite lenses in harzburgite and in the overlying dunite. Further work described here has examined PGM from other lithologies in the ophiolite in order to identify primary magmatic and secondary assemblages.

The least altered minerals in the ophiolite are chrome-spinels and clinopyroxenes. PGM within these minerals are most likely to be unaffected by alteration. Olivine and orthopyroxene have always been observed to be 75–100% altered and silicates interstitial to the chrome-spinels in chromite-rich lithologies are completely altered to serpentinite or chlorite.

The chrome-spinels enclose the sulphur-bearing PGM, laurite. PGM within the clinopyroxenes are Pt and Pd-bearing Ni, Cu, Au, sulphides and Pb alloys representing a new assemblage of PGM previously unknown to Shetland or other ophiolite complexes. The major PGM interstitial to the chromite in the chromite-rich lithologies are arsenides and antimonides. PGM in the serpentinised silicate associated with clinopyroxene include Pt and Pd arsenides, antimonides and tellurides.

PGM, associated with serpentinite, interstitial to both chrome- spinel and clinopyroxene indicate the presence of As and Sb which may have concentrated at the final stages of crystallisation. Geochemical reconnaissance shows that high As and Sb levels occur along fault zones and have been introduced during or after ophiolite emplacement (Lord and Prichard, 1989). The PGM may have been modified at this time.

Identified here are primary magmatic sulphide-bearing PGM and secondary As, Sb and Te-bearing PGM.

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5.7

THE MINERALOGY AND PARAGENESIS OF Pt, Pd, Au AND Ag-BEARING ASSEMBLAGES AT CLIFF, SHETLAND

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The PGE-rich locality at Cliff, in Shetland, lies within a chromite-rich dunite lens in harzburgite, close to the serpentinised basal thrust of the ophiolite. The different lithologies carry different ore assemblages.

Primary chromite-rich and -poor dunites contain an oxide assemblage of chromite, ferri-chromite and magnetite; a Ni-Fe-S assemblage of pentlandite-heazlewoodite-millerite, + Ni arsenides, breithauptite and minor Cu sulphides and native Cu. The enclosing harzburgites show a similar assemblage but with sparse sulphides.

At the basal thrust the harzburgites are totally serpentinised and carry altered chromite and a different Ni-Fe-S assemblage of pentlandite-pyrrhotite-violarite together with chalcopyrite, niccolite and very rare native Cu.

Other than trace amounts of native Au in the basal serpentinite all of the characterised precious metal-bearing minerals are found in dunites. Pt, Pd, Au and Ag-bearing minerals, including tellurides, arsenides, antimonides, native metals, alloys and oxides (ochres), are found as discrete inclusions within chromite, ferri-chromite rims and in the altered silicates.

Paragenetically the earliest assemblage comprises small rounded, less than 2 μm, Pt telluride, Pd telluride and Au telluride grains within discrete 5-20 μm Ni-Fe, Ni or Cu sulphide inclusions in chromite. These inclusions lie in rows or are collected together into clusters.

This assemblage is different from the native Au, Au-Pd, Au-Cu, sperrylite, geversite, palladium antimonide association found with pentlandite, nickel arsenides, breithauptite and Ir-, Rh- and Os- bearing PGM, located in silicate infilled fractures cross cutting chromite, within voids in ferri-chromite or most extensively within the altered silicate matrix. This latter assemblage is the main PGM carrier.

Discrete Au > 10 μm in silicates has a high fineness core with Au-Cu alloy rims. All Au-bearing minerals are Ag-poor but trace amounts of native Ag intergrown with native Cu are present in Cu sulphide or heazlewoodite. Pd antimonides alter to Pd ochre and sperrylite, along its cleavage, to Pt, Fe, Cu, Ni oxides probably as the result of supergene alterations.

5.8

PLATINUM-GROUP MINERALS IN CHROMITE-BEARING ULTRABASIC ROCKS OF THE BRAGANÇA MASSIF, N. PORTUGAL

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The Bragança Massif is one of the Precambrian complexes of N.W. Iberia. It is divided into a series of nappes thrust over a Silurian parauthochthon. The lower nappe consists of metagabbros and metasediments of amphibolite grade metamorphism, thought to be of ophiolitic origin (eg. Pereira, 1986). The upper nappes include ultrabasic rocks consisting of layered dunites, peridotites, pyroxenites and hornblendites. These ultrabasic rocks have undergone granulite facies metamorphism (Munhá and Ribeiro, 1986) and later serpentinisation.

Chromite found within the dunites is exposed in over forty small quarries. The chromite occurs in the dunite both as an accessory phase and concentrated in layers up to 10 cm thick, with as much as 85% chrome-spinel.

Platinum-group minerals (PGM) were first described in the Bragança ultrabasics by Cotelo-Neiva (1948). Oil-immersion reflected light microscopy and qualitative element analyses on an SEM were used for an initial search for PGM. These revealed predominantly euhedral Os-, Ir-, Ru-, Rh- and Pt-bearing inclusions associated with some of the chromite grains including one pure laurite grain devoid of Ir and Os. Composite grains, have also been found; in one case, laurite contains Ru-Mn patches which lack sulphur. The high grade metamorphic and serpentinisation history of the chromites does not appear to have effected the PGM inclusions within the chromite grains.

The results of whole rock platinum-group element analyses from different localities are also presented, with 11.5 ppm total PGE in one chromitite sample.

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5.9

NOBLE METAL MINERALIZATIONS IN LOWER PALAEOZOIC OPHIOLITES IN NORWAY

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Results from projects on platinum group element (PGE) and gold mineralizations in Lower Palaeozoic ophiolites in the Caledonian orogen in Norway are presented. The following types of mineralization have been found:

1) Os–Ir–Ru±Pt (up to 4 ppm total PGE) associated with chromite in podiform chromite mineralizations in isolated ultramafic fragments of ophiolites (e.g. Osthammeren, Feragen).

2) Os–Ir–Ru–Rh–Pt–Pd (up to 8 ppm total PGE) associated with chromite in dunitic dykes which cut mantle tectonites in the Leka ophiolite.

3) Pt–Pd–Au±Os±Ir±Ru±chromite±Fe–Ni–Cu sulphides (up to 2.25 ppm total noble metals) in stratiform enrichments in ultramafic cumulates (Leka and Lyngen ophiolites).

4) Pt–Pd (–Os–Ir–Ru–Rh–Au) (up to 15 ppm total PGE) associated with Fe–Ni–Cu sulphides at high levels in the Karmøy SSZ ophiolite (Fæøy) and Gjersvik ensimatic island arc complex (Lillefjellklumpen).

5a) Au±(Pd) (up to 1–5 ppm Au) mineralization associated with Fe+Cu±(Ni±Pb) sulphides in ophiolitic gabbros on Leka, Bømlo and in the southwestern Trondheim district.

5b) Minor auriferous occurrences (up to 1 ppm Au) of Fe–Cu–Zn sulphides in the sheeted dykes of ophiolite fragments in the southwestern Trondheim district.

The listed mineralizations comprise orthomagmatic types, either directly derived (1, 2, 3) or remobilized to varying degrees (4) as well as epigenetic, structure-controlled deposition (5) the age and derivation of which is highly uncertain.

The projects have been supported by the Royal Norwegian Council for Scientific and Industrial Research (NTNF).

5.10

PGE-GEOCHEMISTRY OF THE ULTRAMAFIC ROCKS OF THE LEKA OPHIOLITE COMPLEX, NORWAY

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The Leka ophiolite complex exhibits two contrasting types of PGE enrichment: Enrichments (up to 8 ppm total PGE) associated with dunitic dykes and veins that cross-cut polyphasally deformed harzburgite of assumed mantle affinity. The relatively high PGE values of these dykes, which are interpreted as feeder dykes to the ophiolitic magma chamber, suggest that the parental magma precipitated PGEs en route to the ophiolitic magma chamber. This is confirmed by the presence of stratabound enrichments (up to 2 ppm total PGEs) close to the base of cyclic units within the cumulate part of the complex. Olivine analyses demonatrate marked resetting to highly forsteritic compositions (Fo_{92}) at the base of the cyclic units suggesting that the cyclicity of the rocks is due to input of very magnesium-rich (20% MgO) parental magmas.

The rocks of the layered series exhibit both Os-Ir-Ru as well as Pt- Pd enriched PGE patterns. While the Os-Ir-Ru enriched patterns are associated with Cr-spinel-rich samples, the Pt-Pd enriched patterns are found in samples relatively rich in disseminated Ni-sulfide. Detailed sampling across a 5 meter thick Cr-spinel-rich horizon shows that Ni-sulfide-enriched samples above the horizon exhibit much stronger Os-Ir-Ru depletion than similar samples below the same horizon, which may be attributed to the strong extraction of these elements during Cr-spinel crystallization.

5.11

PLATINUM-GROUP MINERAL INCLUSIONS IN OPHIOLITIC CHROMITITE FROM THE OSTHAMMEREN TECTONITE BODY, NORWAY

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Chromitite bearing ophiolitic tectonites ranging in size from less than 0,01 km^2 up to 15 km^2 are evenly distributed mainly in one single thrust nappe which crops out along the borders of the Trondheim Nappe Complex in the central parts of the Norwegian Caledonides. The 0,05 km^2 Osthammeren serpentinite lens in the eastern Trondheim region contains massive and schlieren type chromitite-ore with a high Cr/Al-ratio (Cr/Cr+Al=0,90 in fresh, unaltered chromite) indicating a relatively deepseated origin.

This chromitite-ore has been shown to be unusually rich in different platinum-group minerals (PGM). The PGM inclusions occur in two distinctly different ways:

1. Os, Ir, Ru and minor Pt occur in primary magmatic, euhedral-subhedral, small (<5 – 20 µm), mainly single-phase inclusions of Os-free laurite, Os-laurite, osmiridium and Pt_2 (Ir, Os)$Fe_{0,65}$. They are totally

enclosed in fresh unaltered chromite. A few PGM-inclusions are however associated with small blebs of Na-bearing hornblende or phlogopite indicating that the presence of volatiles in an early stage may have influenced upon the formation of these PGMs.

2. Purely secondary PGMs, and more uncommonly, primary PGMs which are later partly modified, occur as anhedral – (subhedral), texturally often very complex grains or grain-aggregates with varying size (5–70 µm) and consisting of from one to eight PGM-phases plus Ni-sulphide and Ni-arsenide. These PGMs always occur within, or in contact with, laterformed cataclastic (metamorphic) cracks or very fine fissures, in the primary magmatic chromite grains. The finer fissures are generally tightened by ferrite-chromite, a hydrothermal alteration-product of chromite. The wider cracks are usually serpentine- and chloritefilled and are rimmed by ferrite-chromite against the chromite. Os, Ir, Ru, Rh, Pt and minor Pd are represented in grains of this group, and the secondary PGM-association found consists of Os-free laurite, Os-laurite, erlichmanite, Ir-rich erlichmanite, native Os, iridosmine (in lamellae), osarsite, irarsite, hollingworthite, Rh-rich platarsite, Ru-rich platarsite, sperrylite, (Ir, Rh)SbS, IrSbS, (Ir, Pt, Pb)S_2 (new?), Pd-antimonide (probably stibiopalladinite) plus the associated phases pentlandite, heazlewoodite and niccolite.

The project has been supported by the Royal Norwegian Council for Scientific and Industrial Research (NTNF).

5.12

RELATIONSHIPS OF PLATINUM-GROUP MINERALS-BEARING CHROMITE MINERALIZATION TO VOLCANIC STRATIGRAPHY IN THE BOBARIS OPHIOLITIC COMPLEX, SOUTHEASTERN KALIMANTAN (INDONESIA)

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Several minor chromitite occurrences, with or without platinum-group minerals (PGM), were recently discovered in suprasubduction zone ophiolites in the Bobaris massif in southeastern Kalimantan, Indonesia. Ophiolitic magmatic rocks associated with the mineral occurrences, 55 in all, are characterized by a variety of textural rock types varying from hydrolized and tectonized harzburgite and pyroxene peridotite or layered-cumulate pyroxene gabbro and gabbrodiorite to massive gabbro and norite. The cumulates are commonly intruded by dike-like bodies of basic volcanics and plagiogranites. Fe-rich ultramafic pegmatoids commonly replace the more felsic cumulates and are locally contained in intercalated leuconorite layers.

The range of chromite and associated PGM is small, but it is systematically related to lithology. Very generally, Cr-rich, Al-poor chromite spatially associated with mafic to ultramafic rocks comprises coarse-grained disseminations or small massive pods and pockets, and more rarely, low-grade disseminations of Al-rich chromite in coarse-grained gabbroic matrix. At deeper levels, mineralization comprises mainly fine-grained disseminations of Cr-rich chromite in harzburgite and dunite. Field observations indicate that platinum very generally lies in the mantle section, in magmatic rocks, and in pneumatolytic and hydrothermal inflows. In the mantle section, laurite-group minerals are found to be closely associated with Cr-rich chromite that forms irregularly distributed podiform massive accumulations in hydrolized ultramafic tectonites.

Field relations indicate that the Bobaris ophiolite is a product of both oceanic island arc magmatism and back-arc spreading. Data from the investigated area also indicate that Cr- and PGM-bearing ultramafites in the complex are associated with regionally extensive, Middle to Late Cretaceous or younger, felsic magmatism.

5.13

Se- AND Pd-CONCENTRATIONS IN CU-NI-SULFIDES/ALLOYS FROM ULTRAMAFIC ROCKS IN THE ACOJE OPHIOLITE BLOCK, ZAMBALES, PHILIPPINES

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A simultaneous enrichment of Se, Pt and Pd for Pt/Pd-rich magmatic sulfide deposits and Se/S > mantle values as a possible indicator of Pt potential was recently suggested by Eckstrand (1988). Secondary Pt–Pd-intermetallic phases were found in Cu–Ni-sulfide enriched black serpentinized dunites of the Acoje ultramafics near the mantle/crust boundary.

Se, analysed by INAA, is concentrated in sulfide rich black dunites up to 9 ppm, in sulfide-poor green dunite less than 1 ppm and in massive gabbro up to 2 ppm. Hand picked sulfide concentrates show Se-concentrations of 32 and 130 ppm, indicating a S-Se correlation. Se/S ratios in the order of $10^{-3\,-\,-4}$ is similar to the Se/S mantle ratio and do not show influence of hydrothermal alteration. Protonmicroprobe (PIXE) analyses of pentlandites, chalcopyrite, their alteration products confirmed an Se-occurrence as solid solution. Chalcopyrite in Pt–Pd-bearing ultramafics contain 150 to 280 ppm Se, Ni-enriched chalcopyrites show increased Se-concentrations of up to 2300 ppm, pentlandites contain 390 to 470 ppm Se, similar to Se in pentlandites from the Stillwater Complex. Pd in the order of 50 ppm has been detected only in a few pentlandite grains. Secondary native Cu however shows inhomogeneous distributed Pd-concentrations varying from below the detection limit up to 1.6 wt.%, confirming that these noble metals are reconcentrated during hydrothermal processes.

Se/S ratios in sulfides correspond to Se/S ratios in bulk analyses suggesting that all Se occurs as solid solution within Cu-Ni sulfides. Se/S ratios in mantle range as well as high Se-concentrations in Acoje ultramafics combined with S-isotope data suggest an igneous source for both S and Se. A correlation of Se, Pt and Pd can be confirmed for this ophiolitic environment.

REFERENCE: *Eckstrand, R.O.* (1988) Selenium in magmatic nickel and platinum deposits: indicator of sulphur source and platinum enrichment. Goldschmidt Conference, Baltimore, 11-13 May, 1988 (abstr.)

6. PLACER DEPOSITS

6.1

PROVENANCE OF PLATINUM NUGGETS IN TULAMEEN PLACER DEPOSITS

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Electron-microprobe studies of oxides and silicates coexisting with Pt–Fe alloys in rocks of the Tulameen ultramafic complex and in nuggets from placer deposits of the region provide a unique signature of the source of the nuggets, even though differences exist in the nature and dimensions of the platinum group minerals. In platiniferous chromitites from the dunitic core of the complex, the principal Pt–Fe alloy has compositions lying near the center of a triangle bounded by tetraferroplatinum (Pt_2Fe_2) – tulameenite (Pt_2FeCu) – ferronickelplatinum (Pt_2FeNi), in contrast to placer nuggets which contain predominantly isoferroplatinum (Pt_3Fe). The nuggets contain chromites with $Cr/(Cr+Al) = 0.79–0.81$ and $Fe^{+2}/(Fe^{+2}+Mg) = 0.66–0.41$, compatible with spinel compositions found in chromitites and dunites forming the core of the Tulameen complex but distinct from spinels in olivine and hornblende clinopyroxenites nearer the margin of the intrusion. Spinels in many of the latter rocks are also enriched in Fe^{+3} which may indicate more oxidizing conditions of crystallization. Nugget olivines (Fo_{93}– Fo_{96}) are distinctly more forsteritic than olivines in either olivine clinopyroxenites (Fo_{83}–Fo_{91}) or dunites (Fo_{88}–Fo_{91}) but closely match olivines enclosed within chromitite layers (Fo_{92}– Fo_{95}). Such unusually magnesian compositions may be rationalized by high-temperature exchange of Mg and Fe between chrome spinel and olivine during subsolidus re-equilibration in a chromite-rich host. These results unequivocally pinpoint chromitite horizons in the core of the Tulameen complex as the ultimate source of placer platinum, and demonstrate both the sensitivity of spinel and olivine solid solutions to the environment of magmatic platinum precipitation and to their potential as aids in mineral exploration.

6.2

PLATINUM GROUP MINERALS IN QUATERNARY GOLD PLACERS IN THE UPPER CHINDWIN AREA OF NORTHERN BURMA

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A system of five Pleistocene terraces in the Chindwin Basin of Northern Burma has been investigated on its Gold and PGM potential. The terraces were unconformably deposited by the Chindwin and Uyu rivers on the Tertiary of the Chindwin Basin. The latter forms a through between the Indoburman Ranges in the west and the former volcanic arc in the east. The geological setting is due to the subduction of the Indian Plate under the South East Asian Block, creating detachment of oceanic crust (ophiolites) to numerous places around the northern part of the Chindwin Basin.

From different placer deposits Platinum Group Minerals have been investigated by optical microscopy, scanning electron microscopy, and electron microprobe.

The main minerals are Pt–Fe-alloys and Ru–Os–Ir-alloys with a ratio of about 1 : 1. The morphology of the crystals allows mostly a rough difference between these two types of minerals. Very rare as isolated grains appear Tulameenite, Isomertieite, Sperrylite, Laurite, and Irarsite. Different PGE-sulphides, -arsenides, -tellurides, -antimonides, and some unnamed minerals occur as small inclusions in Pt–Fe-alloys rather than in Ru–Os–Ir–alloys.

The probable genesis and origin of the PGM will be discussed.

6.3

PLATINUM-GROUP MINERALS FROM THE DURANCE RIVER ALLUVIA, FRANCE

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Platinum-group minerals (PGM) were found, during gold recovery, in the Durance river alluvia near Peyrolles (Bouches-du-Rhône). The PGM grains of average size 130 x 160 microns are strongly flattened (mean thickness 50 microns). Crystal faces are still observable on (Os,Ir,Ru) alloys but rarely on (Pt,Fe). The concentrate consists primarily of isoferroplatinum with minor Os-, Ir-, Ru-bearing alloys, and of Au–Ag–Cu alloys. The following minerals belonging to Os–Ir–Ru system were observed: iridium, iridosmine, osmium, ruthenian osmium, osmian ruthenium and rutheniridosmine (very rare). Iridium and iridosmine are the most frequent. All these phases are devoid of inclusions except iridium which shows exsolutions of Ir-bearing isoferroplatinum and a Pt–Fe alloy. Isoferroplatinum contains numerous inclusions of alloys, sulphides, arsenides, tellurides (frequently in a complex intergrowth) and partly devitrified silica glass droplets. Most of the non-silicate inclusions also exhibit a drop-like shape indicating their original entrapment in a liquid state.

Euhedral crystals (20 microns) of cuprorhodsite, $Cu(Rh,Ir,Pt)_2S_4$, are associated with bornite included in Pt_3Fe. Rarely, Pd–Cu sulphides and Pd tellurides appear in this association. The complex arsenide droplet-like inclusions in Pt_3Fe are composed of Pt-bearing guanglinite, $(Pd,Pt)_3As$, and of a Pt, Cu-arsenide with M/As ratio equal to 8.3. Independent grains of a Pt, Cu intermetallic compound were found.

The composition of the Au,Ag,Cu alloys is close to tetraauricupride, AuCu. Sometimes Sn (up to 3 wt.%) and Ni (up to 1.9 wt.%) concentrations are observed. Shandite, $Ni_3Pb_2S_2$, and (Ni,Pt)Sn inclusions were found in Au,Ag,Cu alloys. Rarely, alloys beloning to the ternary Au–Pt–Cu system were detected.

Silica glass inclusions in Pt_3Fe have the composition of basalt, basaltic andesite, andesite and dacite. The low-TiO_2 content of these inclusions indicates an orogenic-like character. Three magmatic series were defined on the basis of K_2O: low-K tholeiite, calc-alkaline and shoshonite. Similar magmatism is known in Paleozoic formations, in Eocene-early Oligocene turbidic sandstones and more recently as a calc-alkalic/shoshonitic magmatism (Oligocene to near recent).

7. PGE IN OTHER GEOLOGICAL ENVIRONMENTS (OCEAN FLOOR, METEORITE EJECTA, ETC.)

7.1

PGE IN MID-OCEAN RIDGE VOLCANIC EXHALITES: A MAJOR FRACTIONATION OF PGE FROM GOLD

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Core and dredge samples of sulphide-rich sediments and hyrdothermal precipitates from the TAG hydrothermal area of the Mid-Atlantic Ridge and the Explorer Ridge on the Juan de Fuca plate were analysed for Ir, Pd and Au by radiochemical neutron activation analysis. The objective of the research was to establish a data base from which the mobility of PGE in hot, water-rich fluids could be assessed and the implications for ore deposition from such fluids evaluated.

Results indicate that Ir and Pd are typically 0.2 ppb and 2 ppb respectively in sulphide-rich precipitates from MOR hydrothermal precipitates. In contrast Au may reach ppm levels in such materials, although values in the 100 to 200 ppb range are most frequently observed. These abundances constitute a substantial enrichment of Au relative to the PGE in comparison with abundances of these metals typically found in mid-ocean ridge basalts (MORBs). From the literature MORBs have average Au/Ir ratios of approximately 20 in contrast to the ratio of about 1000 as a lower limit for black smoker-related precipitates analysed in this study.

Several petrological and experimental lines of evidence argue that MORBs were sulphur-saturated during magma generation and that an immiscible sulphide fraction, probably PGE-rich, remains in the mantle residue. Hence, MORBs are noble metal-poor, especially with respect to PGE. MOR fluids are thought to constitute hot , rock-equilibrated, modified sea-water solutions capable of substantial leaching of solute from the rock column. Consequently, MOR fluids should reflect the low Ir and Pd contents of the rock column.

Average Au content of MORBs is approximately 1 ppb so that the rock column is not enriched in Au. The generation of fluids which precipitate solids carrying 200 ppb Au is apparently dependent on efficient mobilization of Au from the rock column, high Au solubility in hydrothermal fluids, and efficient mechanisms of coprecipitation of Au on sulphides. Significant differences in parameters such as these are suggested as the cause of strong PGE–Au fractionation seen in precipitates from MOR settings.

7.2

PLATINUM-GROUP METALS IN FERROMANGANESE CRUSTS FROM PACIFIC SEAMOUNTS

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Marine ferromanganese deposits have been known to contain abundant cosmogenic particles for about twenty years, yet ferromanganese crusts on Pacific seamounts have only been recently found to contain Pt in nearly ore-grade abundance. In our initial investigation of Pt-group metals in these deposits, we stratigraphically sampled a 94-mm thick ferromanganese crust from a Cretaceous seamount in the Hawaiian Archipelago that reveals the history of crust accumulation from 82 million years before present (Myr BP), the ^{40}Ar–^{39}Ar age for the seamount. The crust is a 3-component mixture of authigenic ferromanganese oxides, phosphatic limestone and aluminosilicate detritus primarily consisting of fine-grained quartz and plagioclase feldspar. Bulk platinum concentrations range from 100 to 1800 ppb, and positively correlate with the Fe oxide component. A Pt/Al depth profile shows two broad but distinct enrichment horizons that SEM studies reveal to contain Fe–Ni-rich spherules of cosmogenic origin. Detailed Pt and Ir depth profiles by laser abaltion-ICP-mass spectrometry confirm the Pt- and Ir-rich horizons. Pt and Ir concentrations of up to 4 ppm and 40 ppb, respectively, are found within individual spherules. Pt/Ir abundance ratios of up to 200 suggest either Ir loss or Pt enrichment during submarine weathering (oxidation) of the Fe-rich spherules. Laboratory experiments using ^{191}Pt and ^{192}Ir radiotracers are currently underway to test the relative mobility of these two metals in the ferromanganese oxide – sediment – seawater system, which could have implications for the marine geochemistry of Pt and Ir and for cosmic flux and bolide mass estimates based on Ir abundances in marine deposits.

Using an average crust accumulation rate of 1.14 ± 0.02 mm/Myr, the basal intervals of the Pt/Al enrichment horizons correspond to approximately 36 and 65 Myr BP, the age of the Eocene-Oligocene (E–O) and Cretaceous-Tertiary (K–T) boundaries. Phosphatic limestone inclusion horizons found in the lower portion of the crust probably represent the Eocene-Paleocene and late Cretaceous "phosphorite giant" depositional episodes when the seamount was within ±10° of the equator. Independent dating of the phosphatic limestone by ^{87}Sr–^{86}Sr geochronometry confirms the predicted 38 Myr BP age of the Eocene phophorite inclusions, but yields anomalously young ages for vein-type deposits within lower crust layers and the underlying basalt. Further dating of this crust by ^{230}Th, ^{10}Be, Sr and O isotopic methods is planned, as well as efforts to obtain similar Pt-group stratigraphy on crusts from other Pacific seamounts.

7.3

THE URANIUM-GOLD-PLATINUM GROUP ELEMENT ASSOCIATION FROM THE GREATER BEAVERLODGE AREA OF NORTHERN SASKATCHEWAN: A NEW GEOLOGICAL ENVIRONMENT FOR PLATINUM GROUP ELEMENT MINERALIZATION

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Significant levels of Platinum-Group Element (PGE) mineralization were discovered in the Greater Beaverlodge mining camp along with uranium mineralization at the Nicholson #2 zone almost forty years ago. The Nicholson #2 zone represents the type-area for this Unconformity-Related Uranium-Gold-PGE association.

Our studies have shown that the uranium, gold and platinum group element mineralization is confined to extensively fractured, carbonate infilled and hematized Proterozoic calcareous and psammitic metasediments. Studies in the Nicholson Bay area revealed that anomalous levels of PGE are found only where the uranium-bearing fracture zones are in the immediate vicinity of peridotites. Chondrite-normalized PGE profiles of the Beaverlodge mineralization are very similar to profiles from intrusions of a tholeiitic origin. These findings along with the anomalous levels of chrome in some of these hydrothermal environments clearly point to a mafic-ultramafic source for the PGE.

Detailed geochemical and mineralogical studies have shown that Se, Bi and Sb are very important pathfinder elements. Approximately fifty percent of the metallic phases identified in this study are selenides and along with Sb- and Bi-minerals are the primary platinum group minerals. Gold and Au–Pd and Au–Ag–Pd alloys are also important hosts for PGE.

The findings from our detailed geochemical and mineralogical studies and their significance for future exploration for this new type of precious metal mineralization will be discussed.

7.4

MOBILIZATION OF PLATINUM METALS BY DIAGENETIC FLUIDS ALONG THE LAKE ACRAMAN METEORITE EJECTA HORIZON, SOUTH AUSTRALIA

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The 0 to 40 cm thick Lake Acraman Meteorite Ejecta Horizon occurs in greyish red shales and slightly deeper water greenish grey shales of the Late Precambrian Bunyeroo Formation. The horizon consists of a basal breccia layer with clasts ranging from sand-size up to 30 cm overlain by a coarse to median sand unit grading upwards into a fine muddy sand. Evidence for an impact origin includes the abundance of shattered mineral grains, shock lamellae in quartz, small shatter cones on clasts and a PGE anomaly. Where the host shales are greyish red, the ejecta horizon is invariably surrounded by an envelope of pale green shales from one centimeter up to several metres in width.

Whereas background values (40 samples) for the greyish red shales are 0.82±0.40 ppb Pt, 0.44±0.16 ppb Pd, 0.026±0.020 ppb Ir, and 0.107±0.68 ppb Au, ejecta horizon samples contain up to 274 ppb Pt, 7.68 ppb Pd, 2.02 ppb Ir and 5.31 ppb Au. The pale green shales are variably enriched in Pt and Au which correlate strongly with Cu, reaching a high of 313 ppb Pt in a sample with 1.2 wt.% Cu. They are also enriched in Ir, Pd, Ru, Ni, V, Co and Zn and strongly depleted in Fe. It is suggested that the ejecta horizon was an aquifer for low Eh fluids; interaction of these fluids with high Eh, Cu–V–PGE-bearing fluids circulating in the red shales led to precipitation of the ore metals.

Although no ore-grade PGE values have yet been documented, this study has major implications for the mobility of the PGE by low temperature fluids as well as for Ir enrichments at the K–T boundary.

7.5

PLATINUM CONCENTRATION IN FERROMANGANESE SEAMOUNT CRUSTS

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Ferromanganese crust samples collected from Central Pacific seamount areas can be distinctly enriched in Pt. The crust growth is controlled by the conditions of the oceanic water column according to the laws of colloidal chemistry. Within encrustrations > 4 cm two manganese crust generations of different age ranges have been indentified. The older generation is generally richer in Pt than the younger one. The bulk Pt concentration varies between 0.14 and 1.02 ppm. Compared to the upper continental earth's crust, the ferromanganese material contains about 100 times more Pt. A model to explain the Pt values measured in seamount crusts will be presented. Thermodynamic approaches are based on the presumption that the Pt tetrachloro-complex is the prevailing species under seawater conditions. A precipitation of Pt in seawater may take place if this complex is decomposed by reduction of the divalent Pt cation to the elemental state. This reaction might be combined with MnO_2 precipitation caused by oxidation of dissolved Mn. However, the calculations show that the process is only possible under the conditions of a more pronounced paleo oxygen-minimum zone. A further mechanism might be surface adsorption of anionic Pt chloro-complexes onto positively charged amorphous iron hydroxide particles. The influence of cosmic spherules on the Pt content of ferromanganese crusts was also checked. In consideration of the average Pt values of iron meteorites the relative quantity of the discovered spherules is significantly too low to explain exclusively the Pt content of the crust samples.

7.6

HYDROTHERMAL PLATINUM-PALLADIUM-GOLD MINERALIZATION ASSOCIATED WITH URANIUM VEINS, NORTHWEST TERRITORIES, CANADA

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Sporadic high concentrations of Pt, Pd and Au occur in uranium-bearing veins near the unconformity between early Proterozoic felsic volcano-plutonic basement and middle Proterozoic continental siliciclastic sediments of the Hornby Bay Group. Concentrations range from 5 to 42 ppm Pt, 4 to 57 ppm Pd and 1 to 65 ppm Au. Os, Ir, Ru, and Rh levels are below detection limits. Veins carrying Pt, Pd and Au are thin and sparsely distributed in a granite host in proximity to a major fault. No candidate for a possible igneous source rock for Pt and Pd is exposed in the area. The veins contain a wide variety of minerals; Cu-sulfides, Cu–Fe sulfides, Cu–Bi sulfides, Ni–Fe sulfides, pyrite, galena, sphalerite, Co-sulfarsenides, native bismuth, barite, uraninite, pitchblende and coffinite occur with Pd-tellurides, Pd–Bi tellurides, Rh sulfarsenides, Pd–Au alloy, electrum, sylvanite, Ag–Pb tellurides and Ag–Pb–Bi tellurides. Textural relationships suggest that minerals carrying platinum-group and other precious metals are affiliated with sulfides rather than uranium minerals.

Pt–Pd–Au mineralization appears to be epithermal in character. Pt and Pd enriched character of the veins clearly indicate the higher solubility of these elements over Os, Ir, Ru and Rh at low and intermediate temperatures. Preliminary thermodynamic considerations of the enrichment of Pt, Pd and Au compared to Os, Ir, Ru and Rh suggest that the Pt–Pd–Au mineralization can be explained by interaction of an oxidized acidic solution with reduced neutral solution. The unconformity, characterized by a paleo-lateritic profile and a pronounced cross-stratal permeability afforded by faulting provide a favourable environment for such a redox controlled depositional conditions.

8. MINERALOGY

8.1

MINERALOGY OF PLATINUM-GROUP MINERAL INCLUSIONS IN CHROMITITES OF THE FINERO MAFIC-ULTRAMAFIC COMPLEX (IVREA-ZONE, ITALY).

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In the Finero area of the Ivrea Zone (Western Alps), subcontinental mantle is exposed intruding amphibolitic to granulitic continental crust. It was emplaced probably in the late hercynian age and equilibrated under deep-crust conditions. Abundant phlogopite occurs in the mantle rocks as a result of "alkaline-fluid metasomatism" during the uplift into the crust. Small size chromitites have been recently discovered in the marginal zones of the mantle body. Chromite is abnormally high in Ti, and textural relations to silicates suggest that chromitites were partly formed by reaction between restitic mantle and the metasomatizing fluids.

Minute (<20 μm) inclusions of platinum-group minerals (PGM), and base-metal sulfides (BMS) and alloys (BMA) containing platinum-group elements appear to have been trapped during the growth of chromite crystals. The PGMs are laurite, metallic Ir and Ir–Rh–Cu sulfides with variable stoichiometries. The PGE-bearing BMS are rhodian pentlandite, rhodian millerite, iridian digenite, and unknown Ir-rich Ni–Fe–Cu sulfides with stoichiometry close to MS. The BMAs consist of the associations: Cu–Rh, Cu–Pt, Cu–Pb–Rh and Pb–Rh.

Compared with other investigated occurrences dominated by Ru–Os–Ir alloys and laurite, the PGE-mineralogy of the Finero chromitites indicate higher sulfur fugacity of formation. In addition, microprobe analyses revealed the presence of appreciable amounts of Ag and Pb in many of the PGE-phases. These features are unusual for the chromite-forming system and possibly are to be related with the passage of the contaminant "fluid phase" through the Finero mantle.

8.2

LATE-STAGE PGE MINERALIZATION IN CLINOPYROXENITES OF THE OWENDALE INTRUSIVE COMPLEX, FIFIELD, N.S.W., AUSTRALIA

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The PGM mineralization occurring in coarse-grained clinopyroxenites of the Owendale intrusive complex of an alkaline affinity was studied.

The observed PGM were: Pt_3Fe (isoferroplatinum), PtFe (tetraferroplatinum), PtS (cooperite), OsS_2 (erlichmanite), $CuRh_2S_4$ (cuprorhodsite), $CuPt_2S_4$ (malanite), $PtSb_2$ (geversite), $PtAs_2$ (sperrylite), $(Pt,Pd)_4Sb_3$ (genkinite). The platinum-group minerals occur as independent grains (10–20 microns) interstitial to clinopyroxene and are only exceptionally associated with base metal sulphides. The latter are very rare: cobalt-pentlandite being the most common; pyrrhotite, chalcopyrite, pyrite, sphalerite and cobaltite were also observed.

Isoferroplatinum is devoid of Ir and Os; low Rh and Cu concentrations (both up to 0.3 wt.%) are ubiquitous, and Pd content approaches 3 wt.%. Sparse subhedral crystals of (Pt,Fe) alloys are composed of an intimate intergrowth of Pt_3Fe + PtFe resulting from the destabilization of a high-temperature (Pt,Fe) solid solution whose bulk composition was close to Pt_2Fe. Cooperite shows significant Pd concentrations (up to 3.5 wt.%). Erlichmanite is characterized by highly variable Rh (up to 3.8 wt.%) and very high Ir (up to 5.4 wt.%). Extensive solid solution was observed between cuprorhodsite, malanite (26.6 mol.%) and cuproiridsite (22.5 mol.%), as well as between geversite and sperrylite. The maximum observed solubility of $PtSb_2$ in sperrylite is 32.2 mol.%, whilst 33.0 mol.% of $PtAs_2$ appears in geversite.

PGM crystallized during the final magmatic stages. Sperrylite-geversite solid solution is later than the exsolved subsolidus ilmenite in interstitial magnetite. The maximum stability temperature of the equilibrium assemblage OsS_2 + PtS is of about 860°C at log fS_2 of -1. Base metal sulphides appear even later and replace the PGM. They were consequently not in equilibrium with the PGM minerals.

8.3

THE PROPERTIES OF PLATINUM-GROUP MINERALS FORMED AT LOW TEMPERATURES

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Platinum-group minerals (PGM), notably Pt-Fe alloy, Ir-Os alloy, laurite and erlichmanite, can develop in a lateritic soil. Soil water of sufficiently extreme conditions is able to take disseminated PGE into solution and provide transport until reaching a region of more moderate conditions where the PGE are precipitated to form large PGM. This explains the large grain size of eluvial and alluvial PGM which are frequently two orders of magnitude larger than the PGM found in the host rocks.

It is now becoming clear that this model, proposed to explain the form and distribution of the PGM in the Freetown Peninsula, Sierra Leone, is applicable in other tropical regions. Alluvial and eluvial PGM from Papua New Guinea; Yubdo, Ethiopia; and Kalimantan have similar form whilst those from Sumatra are quite different. This paper distinguishes the mineralogical characteristics of the PGM of these deposits and, in particular, examines the magnetic properties of the Pt-Fe alloys. Many of the Pt-Fe alloy grains from Sierra Leone are magnetised and can be seen to move under the microscope in response to a magnetised needle. Both tetraferroplatinum and isoferroplatinum are reported to occur in placer deposits and tetraferroplatinum is ferromagnetic. Available analyses of the Pt-Fe alloy from Sierra Leone and analyses of alluvial grains from other areas are, however, more closely comparable with isoferroplatinum.

This paper will address the questions:

1) Whether both isoferroplatinum and tetraferroplatinum are present in deposits formed at low temperature.

2) The proportion of the grains which are magnetic, the strength of magnetisation and the identity of these with tetraferroplatinum.

3) The relationship between composition and magnetic properties, including the Curie Temperature and consideration of whether this permits a low temperature origin.

8.4

HINTS AND TIPS FOR FINDING GOLD AND PGMs (ALMOST EVERYWHERE) BY SEM/EMP

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One appraises the possibility of detecting PGMs in ordinary polished sections by systematically using SEM (backscattered mode) and EMP (EDS). A series of ores and rocks analysed for gold and separate PGMs has been used for this. These samples came from ultrabasic rocks from the Bushveld, Sudbury, Stillwater and Nizhniy Tagilsk ultrabasic rocks, and mediterranean Ni-As-Cr ores.

Micron size PGMs and other high Z compounds are detectable at a working magnification of 300x, given optimal conditions for contrast, scanning speed and manual stage motion.

In general, PGMs are sufficiently small and dispersed that representative numbers (corresponding to PGE concentrations) can be obtained by scanning from 1 to 3 polished sections of a few cm^2. Ascertaining the absence or presence of PGMs takes about half an hour per 1 cm^2. In addition, one also has the knowledge of the dimensions and associations of the PGMs and gold.

The described method has allowed for a series of premières of PGM discoveries in N. and S. Spain, N. Morocco, E. Algeria, S. Burundi and S. Belgium. Old prospects in N. Portugal and E. Zaire have also been confirmed and extended.

8.5

Ru/Ta ALLOYS AND Ru/TaC OVERGROWTHS IN PLACER CONCENTRATES FROM THE URAL MOUNTAINS, USSR

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In 1962, C. Frondel published a paper entitled "Non-existence of native tantalum". He determined by X-ray diffraction that the Uralian mineral, previously diagnosed by Walther (1909) to be native tantalum, was in fact a tantalum carbide, as early proposed in 1928 by Goldschmidt. The latter was sceptical about the natural origin of such an odd compound. In his paper, Frondel noticed the presence of "native gold and several tiny, well-rounded grains of a silvery gray metal that gave the X-ray powder pattern of ruthenium". This last find is very important as native Ru is extremely rare, as well as the fact that the Uralian mineral could thus also bear testimony to its own, and its associates', origin.

Native ruthenium particles have been separated from several TaC concentrates collected in the Ural and "Altai Mountains"* before 1909. They have been studied by SEM and EMP. The ruthenium occurs as flat squares, a few µm on a side, which display a microstructure of agglomerated spheres of 0.1 µm diameter. The chemical composition is a solid solution of Ru and Ta, with an average Ta content of 6.3 wt.%. No other PGE are present. The Ru crystals are inter- and overgrown by discrete TaC crystals. They may also form fragile agglomerates of several Ru crystals, which probably represent the "well-rounded grains" observed by Frondel.

None of these data entirely excludes the possibility of an artifact, but the chemical and paragenetical constraints are in favour of a common origin for the Ru-Ta alloy and the Ta carbide.

* *The puzzling locality "Altai Mountains", written on several museum labels, is probably a misreading for "Aktai", a small river flowing out from the Uralian PGM field of Sinaia Gora (Wyssotsky, 1913 and Duparc, 1920).*

8.6

PLATINUM-GROUP MINERALS AND ASSOCIATED OXIDES AND BASE METAL SULPHIDES OF THE MAIN SULPHIDE ZONE, GREAT DYKE, ZIMBABWE

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A detailed mineralogical study has been undertaken of base metal sulphides (BMS), associated PGM and oxides in the Main Sulphide Zone from two holes, one drilled near the axis and the other near the margin of the Darwendale subchamber of the Hartley complex of the Great Dyke.

BMS include pyrrhotite (hexagonal and monoclinic), pentlandite (independent grains and exsolutions in pyrrhotite), chalcopyrite, pyrite and mackinawite (exsolutions in chalcopyrite). Rarely, cubanite lamellae in chalcopyrite and traces of galena included in pyrite were observed. BMS are generally interstitial with respect to silicates or penetrate into pyroxenes along cleavage traces. Pentlandite contains variable Co concentrations (up to 1.6 wt.%), low Cu (0.2 wt.% maximum) and highly variable Pd (up to 0.15 wt.%). Pyrrhotite is always low in Cu, Co and Ni (generally less than 0.1 wt.%). Chalcopyrite contains up to 0.2 wt.% Ni, and less than 0.1 wt.% Co; several analyses showed up to 0.2 wt.% Pd in chalcopyrite. Pyrite exhibits up to 3.1 Co and 0.5 Ni (wt.%).

Platinum-group minerals (PGM) occur as minute inclusions (up to 20 µm) mainly in pentlandite, more rarely in chalcopyrite and pyrrhotite. The PGM association is characterized by the predominance of Bi, Te-bearing minerals. The order of crystallization is: PdTeBi (michenerite) – $(Pd,Pt)(Te,Bi)_2$ (merenskyite) – $(Pt,Pd)(Te,Bi)_2$ (moncheite) – $(Ni,Pd,Pt)(Te,Bi)_2$ (melonite) – Ag_2Te (hessite) – $AgBiTe_2$ (volynskite) – $(Pb,Ag)Bi_2Te_4$ (rucklidgeite) – PbTe (altaite) – $PtAs_2$ (sperrylite) – RhAsS (hollingworthite) – (Ni,Co)AsS (gersdorffite) –(Au,Ag) (electrum). Extensive solid solutions are observed between the melonite, merenskyite and moncheite end-members. The mineral succession reveals that Pd precedes Pt which is followed by Ag and Pb. Furthermore, the Te/(Te+Bi) ratio increases in later minerals in the succession. Arsenides and sulpharsenides appear very late. Final stages are characterized by the appearance of Se-bearing minerals (clausthalite).

The oxides, chromite, loveringite, ilmenite and rutile, occur as intercumulus grains and crystallized from a liquid enriched in incompatible elements. Loveringite, $(Ca,REE)(Ti,Fe,Cr,Mg,Mn,V,Zr)_{21}O_{38}$ contains between 6.6 to 12 wt.% Cr_2O_3 and up to 5.2 wt.% ZrO_2. Rutile is Cr and Zr-bearing (up to 2.0 wt.% Cr_2O_3, 1.3 ZrO_2). Chromium-spinel is enriched in TiO_2 (up to 2.1 wt.%). Ilmenite shows an extensive solid solution with pyrophanite (up to 5.0 wt.% MnO) and contains 0.5 wt.% Cr_2O_3.

8.7

PROTON-MICROPROBE ANALYSIS OF PLATINUM-GROUP ELEMENTS IN SULFIDES FROM BUSHVELD AND SOME CANADIAN NICKEL-COPPER SULFIDE OCCURRENCES

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Concentrations of platinum-group elements (PGE), Se, Te, As, Ag, Cd, Zn, Ga and Ge in pentlandite, chalcopyrite and pyrrhotite from a variety of settings have been determined by proton-induced X-ray emission (PIXE) microprobe at the University of Guelph. Inclusion-free areas previously examined by SEM were probed using a 15 µm sized proton beam. Beam current ranging from 7.6 to 17.3 nA at 3 MeV was used. Counting time varied from 4 to 22 minutes. Data reduction was done using a computer program GUPIX developed at the University of Guelph. The following results are based on 200 sulfide grains from the Bushveld Complex, Muskox intrusion (Northwest Territories), Rottenstone (Saskatchewan), Namew Lake, Thompson and Cuthbert (Manitoba), Wellgreen (Yukon), and St Stephen, Mechanic and Goodwin Lake (New Brunswick).

Among the coexisting pentlandite, chalcopyrite and pyrrhotite, pentlandite is the only phase that can accommodate detectable levels of Pd, Rh and Ru. Concentrations range up to 566 ppm Pd, 41 ppm Rh and 61 ppm Ru. Se is present in all three sulfide phases and its partitioning among the three phases is equal. In general, sulfides from the PGE-rich occurrences have Se/S ratios greater than or within the mantle range. Sulfides from the PGE-poor Ni–Cu occurrences such as the Thompson, St Stephen and Goodwin Lake where the sulfur is mainly of crustal origin, display depleted levels of Se/S ratios. Ag is present in both pentlandite and chalcopyrite. Almost all the chalcopyrites and most of the pentlandites contain detectable levels of Ag. Concentrations as high as 279 ppm in pentlandites and 160 ppm in chalcopyrites were obtained. Zn appears to partition exclusively into chalcopyrite. Concentrations as high as 4283 ppm are present in almost all the chalcopyrites. Bi, Pb and Te do not appear to have any preference among the three phases. Ga appears to prefer pentlandite whereas chalcopyrite accommodates all the available Ge.

8.8

AN INTEGRATED ANALYTICAL TECHNIQUE ON THE RAPID CHARACTERIZATION OF PLATINUM-GROUP MINERALS IN ORES

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An automated technique utilizing a scanning electron microscope and an X-ray microanalyser equipped with image analysis capability has been developed to characterize platinum-group minerals (PGM) in ores. A high spatial and atomic number resolution backscattered electron detector is used to detect PGM as well as other minerals with high average atomic number. Subsequent distinction and characterization of PGM are made by the X-ray microanalyser. Characterization is made by using a unique series of elements for each class:

Unique elements	*Example*
Pt,Fe	Pt–Fe alloy
Pd,Bi	polarite, froodite
Pt,S	cooperite
Pt,Pd,S	braggite
Pd,S	vysotskite
Ru,S	laurite
Pd,Bi,Te	michenerite, kotulskite
Pd,Te	merenskyite
Pt,Pd,Bi,Te	moncheite
Pt,Bi,Te	maslovite
Pt,As	sperrylite
Pd,As	stillwaterite

Major advantages of this technique are rapid counting, sizing and classification of PGM as small as 0.25 micrometer. Application of this technique to samples from various platinum-group element occurrences revealed that the majority of the PGM particles are very small. For example about 82 % of the PGM particles are found to be less than 1 square micrometer in a sample from the UG–2 chromitite layer of the Bushveld Complex. Only 2 % of the total PGM particles are larger than 10 square micrometers. Even though the grains that are less than 1 square micrometer account for only 15 % of the total volume of the PGM particles, the information is important in determining the optimum recovery methods in mineral processing.

9. ANALYTICAL METHODS, EXPERIMENTAL, ETC.

9.1

NICKEL SULPHIDE FIRE ASSAY FOR THE COLLECTION OF THE PLATINUM GROUP ELEMENTS AND GOLD FROM CHROMITITES USING REDUCED BEAD SIZE.

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Fire assay is a classical method for separation of platinum group elements and gold (PGE+Au) by preconcentrating into collector. In nickel sulphide fire assay, nickel and sulphur are used for the collection of PGE+Au. In the past the authors have successfully reduced the weight of collectors used without affecting the recovery of the elements for silicate material, the result is the elimination of the reagent blank problem. In this work the authors have applied the small bead size to chromitites. Chromitites can be difficult to fuse, and the authors have applied their modified technique to improve the dissolution for the chromitites. This paper describes the application of the reduced bead size to the preconcentration of the PGE+Au from chromitites, by using only 0.5 gram of the nickel which is twenty times less than the weight used by the other fire assay workers.

9.2

QUANTITATIVE TRACE PGE ANALYSES OF PYRRHOTITE, PENTLANDITE AND MILLERITE

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Quantitative ion probe microanalysis, because of its sensitivity and low minimum detection limits effectively addresses the requirements for the determination of the platinum group elements (PGE) in sulphides and arsenides from ores and mattes. The minimum detection limits (MDL) for platinum, palladium, rhodium and iridium are 100, 600, 100, and 200 parts per billion (ppb) respectively. The in depth profiling capability of the ion microprobe allows the identification of subsurface submicron inclusions, resulting in more accurate determinations of the PGEs, which are dispersed in the crystal structure of the sulphides, or are in the form of inclusions of less than 200Å in diameter.

Thus, the mineral carriers of the "invisible" PGEs can be identified, and losses in mineral processing plants can be accounted for. Determined platinum, palladium and rhodium concentrations for pyrrhotite, nickelian pyrrhotite, pentlandite and millerite from some Sudbury ores range from <MDL to 7000 ppb.

9.3

APPLICATION OF Re-Os ISOTOPIC ANALYSES TO PGE DEPOSITS

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The Re-Os decay scheme ($^{187}Re \rightarrow ^{187}Os$) offers a unique opportunity to investigate the genesis of, and directly date, platinum deposits and ultramafic rocks. This decay scheme has not been previously utilized much because Os cannot be analysed by conventional thermal mass spectrometry. However, inductively coupled plasma-mass spectrometry (ICP-MS) is a viable method as it provides the high temperatures that ionize Os (6000°K).

Accordingly, we have modified a traditional ICP-MS unit to analyse Os. Os in solution is placed in a distillation device, oxidized to OsO_4 using H_5IO_6 and this vapor introduced directly into the mass spectrometer. Pt, Re and W, potential interfering isotopes, do not distill over into the ICP-MS and are thus avoided. Parameters such as temperature and reagent have been optimized and we now analyze OsO_4 in a controlled and reproducible manner. Cleaning procedures are in place to avoid memory effects. Re is analysed as an aerosol spray generated by conventional ICP-MS nebulization.

The Re and Os contents are determined most precisely by isotope dilution analyses. To do this, a "spike" of Re and Os is needed that is artificially enriched in the isotopes that are less abundant in nature. Most spikes are utilized in the liquid form, but our spike is a powder that is a weak solid solution of Re, Os in a Ni-sulphide matrix. The spike is added to the sample prior to fire assay or peroxide fusion to ensure complete homogenization of spike and sample.

The solid spike was prepared from metallic Re and Os by a nitric dissolution-thioacetamide precipitation-fire assay technique. Accurate results for the solid spike after this chemical treatment are within the precisions quoted by the suppliers of the metallic spikes. For instance, $^{190}Os/^{192}Os$ quoted by Oak Ridge Nuclear Laboratory is 51.91 ± 2.59; our results for the same ratio are 51.45 ± 0.9 (2 sigma). Other results include $^{187}Os/^{188}Os$: 0.063 ± 0.006, $^{185}Re/^{187}Re$: 17.04 ± 0.41 (both 2 sigma).

Results on a sample from Inco's Frood Mine, Sudbury, Ontario yield an $^{187}Os/^{188}Os$ ratio of 1.229 + 0.008 (2SD). Work is in progress on SARM-7, other standards and samples from various localities.

9.4

STABILITY OF PLATINUM CHLORIDE COMPLEXES IN HYDROTHERMAL FLUIDS

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It is now known that hydrothermal processes may play an important role in the secondary enrichment of platinum. Transport as chloride-complexes has been established for many metals and it is our aim to assess the likelihood of such transport for platinum.

The stabilities of platinum(II)chloride complexes in aqueous solutions are being determined experimentally at temperatures up to 300°C. The experiments involve the dissolution of platinum metal in acidic, saline solutions. Sets of sealed silica glass tubes containing the reagents are heated in fluidised alumina baths under identical, but unbuffered, oxygen fugacities and at fixed pH and a range of total chloride concentrations. The solubility data obtained may be interpreted in terms of the stability of various platinum complexes but do not provide accurate thermodynamic data on solubility.

Experimental conditions were established after calculation of the aqueous speciation of platinum from a review of sparse experimental and theoretical data. These calculations suggest that platinum(II)chloride complexes may be more important than previously thought, although platinum(II)hydroxide complexes, in particular the neutral $Pt(OH)_2{}^0$ species, appear to be more important for most hydrothermal fluids.

Analysis of solutions is by Graphite Furnace Atomic Absorption Spectroscopy employing a 1900°C ashing stage to minimise matrix interferences. Adsorption of platinum onto container surfaces prior to analysis is not a problem in this study due to the low pH of solutions. It has been found that unacidified platinum solutions at concentrations of 0.5ppm or less suffer significant losses over days or weeks.

9.5

PHASE SYSTEMS Fe–Ni–Pd–S AND Pt–Pd–Fe–As–S AND THEIR APPLICATION TO PGE DEPOSITS

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In the present project, sponsored by EEC as part of the Raw Materials Programme, several arsenide-sulphide associations substantial for understanding, exploration and beneficiation of PGE deposits are studied. The system Fe–Ni–Pd–S contains important carriers of Pd in ore deposits – braggite, pentlandite and pyrrhotite. It is studied at temperature levels of 400°C, 550°C, 725°C and 900°C by means of dry charges sealed in silica glass tubes. The synthetized phase assemblages are studied by microprobe analyses.

The system Pt–Pd–Fe–As–S involves the problems of Pt/Pd distribution among sulphides, arsenides and alloys, the solubility of Pt or Pd in various mineral phases or in the sulphide melt as well as the coexistence of Pt/Pd minerals with various iron-containing phases. Its subsystems Pt–Fe–As–S and Pt–Pd–As–S are studied at 850°C and 470°C by the same techniques as in the previous case.

Preliminary phase diagrams for the above systems and temperatures, compositional data for synthetic Pt- and Pd-minerals and data on the solubility of these PGE in base metal compounds will be presented at the conference.

9.6

SULFIDE MELT–SILICATE MELT DISTRIBUTION COEFFICIENTS FOR THE NOBLE METALS AS DEDUCED FROM MORBS

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New analyses of PGEs in coexisting sulfide and glass of MORB sample 526–1 have been obtained by combined instrumental and radiochemical neutron activation analysis of hand picked separates. The sulfide melt-silicate melt partition coefficients (K_d) for Au, Ir and Pd are all on the order of 10^4 (columns 1–3), in agreement with previous estimates based on study of this sample but distinct from the values derived from layered intrusions (e.g., 1).

The data have been used to model the behaviour of PGEs during generation of MORB in its source region. The model assumes that all the PGEs, Se and Cu in the mantle reside in sulfides and that sulfide-saturated melt in the mantle contains 800 ppm S. Starting with a bulk upper mantle composition based on data from mantle xenoliths (2, 3) (col. 4), 20% batch partial melting yields a silicate melt and a residual mantle sulfide having the compositions given in columns 5 and 6, respectively. With the exception of Ir, the melt is similar to the bulk composition 526–1 in terms of both the absolute and relative abundances of the chalcophile elements. This implies that a sulfide similar to that in 526–1 is left as a residue of partial melting to produce MORB and that primitive MORB compositions are determined by their equilibration with that sulfide. In contrast to MORB glass, the relative abundances of PGEs, Se and Cu in boninite (4) (col. 7) closely resemble those of the sulfide that separated from MORB. This supports the model of (4) which holds that while the relative PGE abundances of boninite are controlled by mantle sulfide, no sulfide residue remains after the generation of boninite magma. That the modeling fails to account for Ir abundances supports the possibility that the distribution of Ir is controlled by phases in addition to sulfide.

	SULFIDE	GLASS	K_d	MANTLE	20% MELT	RES.SULF.	BONIN.
	ppm	ppb		ppb	ppb	ppm	ppb
Ir	1.2	0.043	2.79x10^{4}	3.4	0.99	28	<0.23
Pd	32.7	<1.4	>2.34x10^{4}	4.5	<1.23	>37	15
Au	19.0	0.7	2.69x10^{4}	1.01	0.31	8	1.9
Se	421	238	1.77x10^{3}	57	141	249	53
Cu	13%	100ppm	1.30x10^{3}	28ppm	80ppm	10%	20ppm
S	34.6%	890ppm	3.89x10^{2}	200ppm	800ppm*	34.6%*	<54ppm
Se/Au	22	340		56	461	30	28
Se/Pd	13	>170		13	>115	<7	3.5
Cu/Au**	7	143		28	262	13	11
Cu/Pd**	4	>71		6	>65	<3	1.3
Cu/Se	309	420		491	567	417	377
Pd/Au	2	<2		4	<4	>4	8
S/Se	822	3739		3509	5677	1388	<1019

* assumed; ** x10^{-3}

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10. LAYERED INTRUSIONS IN NORTHERN FINLAND

10.1

EARLY PROTEROZOIC LAYERED INTRUSIONS IN THE NORTHERN PART OF THE FENNOSCANDIAN SHIELD

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Early Proterozoic layered intrusions, about 2.44 b.y. in age, are scattered over a large area of the northern Fennoscandian Shield, being distributed in three countries: Finland, Sweden and the Soviet Union. The outcrops vary greatly in size, the smallest being less than one square kilometre whereas the largest occupy an area of several hundreds of square kilometres.

Only one intrusion, the Kukkola intrusion, is encountered in Sweden, whereas, in Finland, the number exceeds twenty. They are concentrated principally in two areas. The first group forms a discontinuous belt, termed the Tornio-Näränkävaara intrusion belt, which crosses northern Finland at the latitude of the northern end of the Gulf of Bothnia and is marked by the Tornio, Kemi and Penikat intrusions and the scattered Portimo and Koillismaa complexes. The second group comprises the Koitelainen intrusion with its satellites and is located in central Finnish Lapland. In the Soviet Union the intrusions are concentrated in three areas: (i) in the Kola Peninsula, (ii) in the Paanajärvi area close to the Finnish border and (iii) on the northeastern side of Lake Onega. The first group includes the Monchegorsk, Fedorova and Panski intrusions, while the second comprises the Kivakka, Tsipringa and Lukkulaisenvaara intrusions. In the Onega area only the poorly exposed Burakovsky intrusion is known.

Examples of all the ore types characteristic of layered intrusions have been found in these intrusions. Chromitite layers are encounterd in the Kukkola, Tornio, Kemi, Penikat, Koitelainen and Burakovsky intrusions, but only one, the Kemi chromitite, is so far mined. The Portimo, Koillismaa, Monchegorgsk and Fedorova intrusions are characterized by the PGE-bearing Cu-Ni-deposits in their marginal series. Mineralized zones enriched in PGE are also encountered in the layered series. Those in the Penikat intrusion and in the Portimo intrusions are the most remarkable and the best known to date. Vanadium-bearing Fe-Ti-oxide layers are encountered in the Koitelainen and in the Koillismaa intrusions, but only one, however, the Mustavaara deposit, has been exploited up until now.

The emplacement of the early Proterozoic layered intrusions in Fennoscandia was part of world-wide igneous activity as suggested by the occurrence of large layered intrusions of almost similar age in the other ancient cratons, i.e. the Jimberlana (2.42 b.y.) in Australia and the Great Dyke (2.46 b.y.) in Zimbabwe. This almost contemporaneous emplacement of these intrusions would suggest a more intimate relationship between the Fennoscandian Shield, Yilgarn Block and Zimbabwean Craton at the beginning of the Proterozoic than at present.

10.2
PGE MINERALIZATIONS IN THE TORNIO-NÄRÄNKÄVAARA INTRUSION BELT, NORTHERN FINLAND

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The PGE deposits of the Tornio–Näränkävaara belt may be classified into three groups: 1. PGE-rich mineralization types which include SJ, AP I, AP II and PV in the Penikat intrusion and the Konttijärvi, Rytikangas and Siika-Kämä mineralizations in the Portimo complex, 2. PGE-bearing sulphide mineralization types in the Portimo and Koillismaa complexes and 3. chromite- and silicate-associated low grade PGE-mineralizations in the Kemi, Penikat and Portimo complexes.

With the exception of SJ, all the types of group 1 are associated with sulphide disseminations and have high PGE-concentrations in their sulphide fraction. The Konttijärvi type is situated in the contaminated marginal series of the intrusion but all the others are typical reefs. They are highly fractionated having high (Pt+Pd) / (Os+Ir+Ru) ratios and rather steep chondrite-normalised profiles. The types of group 2 comprise massive pyrrhotite-dominant and disseminated or massive chalcopyrite-dominant sulphide deposits, which are associated with contaminated marginal series and/ or basement rocks. The PGE-content in the sulphide fraction is lower than in the types of group 1. The chalcopyrite-dominant types are more fractionated than the pyrrhotite-dominant ones. Group 3 is related to ultramafic rocks of the lower parts of the intrusions. The low fractionation degree is manifested by low (Pt+Pd) / (Os+Ir+Ru) ratios and gently sloping chondrite-normalized profiles.

Siika-Kämä, PV and SJ are connected with contact zones between two megacyclic units and they probably have a genetic association with the mixing of two magmas. The PGE-concentrations (AP I, AP II, Rytikangas) of the inner parts of the megacyclic units presumably have a genetical connection with the PGE-enriched intercumulus liquid, which was later filter-pressed to a physically favourable environment, where the PGM and sulphide precipitation took place. The genesis of group 2 and Konttijärvi is related to a contamination process that took place in the basal portions of the chambers during the magma input. In addition to contamination, the mixing of two magmas may have resulted in a high tenor of PGE in the Konttijärvi mineralization. The available sulphur isotope data suggests that the sulphur of the mineralization types of group 2 is magmatic in origin.

10.3
THE ALA-PENIKKA PGE MINERALIZATIONS IN THE PENIKAT LAYERED INTRUSION, NORTHERN FINLAND

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The PGE mineralized zones, named Ala-Penikka mineralizations (AP I and AP II), are located about 250 metres and 340 metres above the base of the megacyclic unit IV of the Penikat layered intrusion, both mineralizations being hosted by plagioclase-augite-bronzite and narrow poikilitic plagioclase cumulates. The megacyclic unit IV commences with peridotitic-pyroxenitic cumulates 0.5–30 metres in thickness. These ultramafic rocks are, in turn, overlain by a thick sequence of gabbronoritic cumulates with some narrow anorthositic interlayers. Gabbronoritic cumulates are composed of plagioclase-augite-bronzite and plagioclase-bronzite cumulates with intercumulus augite, and this sequence has been divided into subzones on the basis of the chemical composition of the augite. In the area of the AP I mineralization a depression structure (pothole) about 300 metres long and 100 metres deep, is encountered. In this structure the AP I mineralization, which is normally 30 cm thick, attains its maximum thickness of 20 metres.

The primary silicate minerals include olivine, bronzite, augite and plagioclase. The most prominent sulfide minerals in the AP I mineralization are pyrrhotite, chalcopyrite, pentlandite and pyrite, whereas in the AP II mineralization they are represented by chalcopyrite, pentlandite and pyrite. The platinum-group minerals identified comprise almost thirty species, the most common ones being Pd–Te–(Bi)-, Pd–As–Sb-minerals and sperrylite ($PtAs_2$).

When the magma,which formed the megacyclic unit IV, intruded into the Penikat layered intrusion its lower part intermixed with the older residual magma. This hybrid magma was slightly lighter than the magma in the lower part of megacyclic unit IV and so it rose upwards. When the magma input calmed down the magma was divided into convecting liquid layers which resulted in the formation of the subzones of megacyclic unit IV. When the subzones below the AP mineralizations consolidated, intercumulus liquid with associated PGE, S, Ni and Cu were squeezed up. This upward migrating liquid was stopped by the poikilitic anorthosite of the AP mineralizations, and sulfides and platinum-group minerals were precipitated. The depression structure developed when some disturbance in the magma chamber caused the unconsolidated cumulate layers to collapse and the fracture zone thus formed acted as a trap for the intercumulus liquid mentioned above and resulted in the thickening of the mineralization in this depression.

10.4

THE PAASIVAARA PGE MINERALIZATION IN THE PENIKAT LAYERED INTRUSION, NORTHERN FINLAND

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The internal structure of the early Proterozoic Penikat layered intrusion can be divided into three principal units: the marginal series, the layered series and the granophyre. The layered series can further be divided into five megacyclic units, which have been interpreted as being attributed to repeated influxes of new magma into the Penikat chamber. Three major PGE-bearing mineralized zones have been found in the layered series. They have been designated as the Sompujärvi (SJ), Ala-Penikka (AP) and Paasivaara (PV) mineralizations according to the site of their initial discovery.

The uppermost of these, the PV-mineralization, has the highest Pt/Pd-ratio. It is located in the transition zone between the fourth and the fifth megacyclic unit. The upper half of the transition zone comprises anorthositic layers and a mixed rock which is composed of anorthositic matrix and darker patches of plagioclase and/or plagioclase-bronzite cumulate. The lower half is principally comprised of leucogabbros and anorthosites.Pegmatoidal rocks are also encountered, especially within the mixed rock. The main host rock for the mineralization is the uppermost anorthosite of the transition zone, disseminated sulphides and associated platinum-group minerals being concentrated in the interstices of this plagioclase orthocumulate. Mineralization has also, however, been encountered in other parts of the transition zone, and sometimes even in the lowermost parts of the fifth mecacyclic unit. The most typical sulphide paragenesis in the mineralization is chalcopyrite-pyrrhotite-pentlandite, whereas the PGM identified are represented by sperrylite ($PtAs_2$), kotulskite (PdTe), merenskyite ($PdTe_2$), isomertieite ($Pd_{11}Sb_2As_2$), stibiopalladinite (Pd_5Sb_2), cooperite (PtS) and braggite

[(Pt,Pd,Ni)S].

The texture, and whole rock and mineral chemistry of the transition zone give a strong impression of magma mixing. The chromium content and the Mg/Fe-ratio of the augite, the An-content of the plagioclase and the whole-rock chromium content increase in the transition zone, as compared with the fourth megacyclic unit, while the Fe-content and the modified differentiation index decrease. It is suggested that the Paasivaara mineralization was formed in the mixing process when the fifth magma pulse was intruded into the magma chamber. Mixing of the new magma with the older residual magma in the chamber caused sulphide precipitation. Mixing and convection were probably turbulent at first, and the sulphides were thus able to "scavenge" the PGE from a great amount of silicate melt. According to their metal ratios the PGE seem to have a close genetic relationship with the fifth magma pulse.

10.5

THE SUHANKO–KONTTIJÄRVI INTRUSION AND RELATED PGE MINERALIZATIONS, NORTHERN FINLAND

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The Suhanko-Konttijärvi intrusion crystallized in the southern chamber of the Portimo igneous complex. It is composed of the larger Suhanko body (ca 15 km^2) and the smaller Konttijärvi body (ca 0.3 km^2). Late Archaean granitoids form the basement to the intrusion. The roof rocks are composed either of similar granitoids, younger mafic sills or a subracrustal sequence of volcanic and sedimentary rocks.

The Suhanko-Konttijärvi intrusion may be divided, from the base upwards, into the marginal series (20–150 m thick) and the layered series (ca 600 m thick). At the base of the marginal series in the Konttijärvi body and in the western end of the Suhanko body, exotic cumulate layers and their fragments are encountered. In addition, chemically analogous sills occur in the basement below the marginal series. These rock types differ from the main intrusion in their much higher chromium content.

The marginal series begins with gabbroic cumulates and continues through pyroxenitic to peridotitic ones, thus denoting reversed fractionation. The lower contact of the intrusion is diffuse and the xenoliths from the basement rocks are common in the marginal series. The lower half of the layered series is mainly composed of plagioclase-bronzite-augite cumulates, and the upper half of plagioclase-augite cumulates. The uppermost cumulates are cut by or mixed with granophyric material.

Three types of PGE mineralizations are identified in the Suhanko-Konttijärvi intrusion: (i) disseminated PGE -bearing sulphide mineralizations in the Konttijärvi and Suhanko marginal series, (ii) pyrrhotite deposits, mostly massive, close to the basal contact of the Suhanko body and (iii) the Rytikangas mineralization in the Suhanko layered series. The PGE grade in the Konttijärvi and Rytikangas mineralizations is much higher than that in the others. Disseminated types of the marginal series are erratic in their distribution, extending from the lower peridotitic layer downwards for some 30 metres to the basement. The newly found Rytikangas mineralization is located about 150 m above the base of the layered series. It is hosted by poikilitic plagioclase cumulate and homogenic plagioclase-bronzite-augite cumulate located below the former. The chromium content of the gabbroic rocks in the layered series reaches its highest value at the level of the Rytikangas minaralization.

Contamination is considered to have played an important role in the genesis of the low grade PGE mineralizations of the marginal series. Further, the mixing of two basic magmas, which is apparent in the Konttijärvi marginal series, may have affected the formation of the higher grade mineralization type of the marginal series.

11. REGIONAL STUDIES

11.1

POTENTIALITY FORECAST MAP FOR BRAZILIAN PLATINUM

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The potentiality forecast maps (PFM) for metals are based on the geological knowledge of the country and the geological environments favourable for the location of metal and/or mineral concentrations. In Brazil, since 1978 such maps are being prepared at different scales in priority regions. PFM for platinum is not made together with others, and is not known to the authors.

Brazil does not produce platinum, imports for consumption each year, and has no projection that includes any production. With this incentive, the map is prepared to a scale of 1 : 5,000,000 to demarcate the possible potential areas in the context of geological knowledge, with petrogenetic and geotectonic criterions. The map thus shows areas of: 1) very high; 2) high; 3) medium; 4) low; and 5) very low, potentialities of the metal. Corresponding regions are: 1) 1%; 2) 10%; 3) 5%; 4) 30% and 5) 54%. of the Brazilian territory. It is estimated that the very high potential area is about 96,250 km^2. Six provinces are defined.

In the light of the PGM associated ultramafic and mafic rocks as primary concentrations (Ni, Cu, Co, Cr, Ti magnetite, sulphides and oxides; PGM ore with byproduct Cu–Ni–Ag–Au); weathered and concentrations of Ni, Co, Cr laterites with residual or mobilised PGM from the ultramafic and mafics; and placer concentrations from weathered zones, with Ir–Os alloys and Pd , also; and Ni–Cu in soils, the geological environments known in Brazil significant for platinum are: 1) Layered ultramafic-mafic intrusions in granite-gneiss and granulite terrains. 2) Synvolcanic layers in greenstone belts and deformed volcano-sedimentary sequences. 3) Intrusive bodies in dominantly meta-sedimentary sequences of the fold belts.

In resume, among the described geological environments, the layered intrusions and serpentinised bodies could be considered as the highly potential areas for PGM in Brazil. The exploration guides, however, seem to be lateritic coverings and derived placers with platinum metal, and/or sperrylite.

11.2

TILL GEOCHEMICAL EXPLORATION METHOD ON PGE IN PERÄPOHJA AND KOITELAINEN, NORTHERN FINLAND

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A research was made to study the dispersion of palladium in the fine fraction (-0.064 mm) of till using two different sampling densities in the Peräpohja and Koitelainen areas. Also the dispersions of tellurium, copper and some other elements, which may serve as pathfinders for PGE mineralizations were compared with the dispersion of palladium.

The extent of the Peräpohja study area is about 12 000 km^2 . The layered intrusions of the Penikat zone are situated in the area (*Alapieti and Lahtinen 1986*). The sampling density in the Peräpohja area is about one sample / 30 km^2 (*Bergström et al. 1983*). Totally 340 samples were analyzed. The Koitelainen study area consists of 4800 km^2 and the sampling density is about one sample / 4 km^2. Totally 1040 samples were analyzed.

Till samples have been dried and sieved. The fraction of <0.064 mm has been used for analyses. The trace and main elements of the samples from Peräpohja area were analyzed with a tape feed emission spectrometer and the Koitelainen area with a plasma emission spectrometer (ICP) using aqua regia digestion (*Chemical Laboratoty, Geological Survey of Finland, SF-02150 Espoo*). Palladium and tellurium have been determined with a graphite furnace AAS after aqua regia digestion and preconcentration by reductive co-precipitation by mercury and stannous chloride (*Kontas et al. 1986*).

In Peräpohja area numerous anomalous samples for palladium have been discovered. A factor analysis using orthogonal varimax rotation was carried out for the analytical data. Factor 1 with high loadings of Pd, Te, Cu (Ni, Co, Mg) reveals the known PGE mineralizations of Ala-Penikka, Konttijärvi, Kilvenjärvi and Siikakämä. Only the Sompujärvi mineralization which doesn´t contain telluride minerals is not revealed by this factor.

In the Koitelainen intrusion many PGE-mineralizations are known. The most significant of these, although still uneconomic, is the magnetite gabbro unit. However, Pd-anomalies in the till fine fraction do not generally coincide with these rocks. A wide Pd-anomaly appears in the eastern part of Koitelainen intrusion where at least one Pd-rich mineralization is known. This Pd-anomaly coincides with the upper main zone of the mafic layered succession (*Mutanen 1989*). Another anomalous area of palladium is situated across the southwestern corner of the Koitelainen intrusion. The adjacent Keivitsa-Satovaara mafic layered complex is known to contain PGE-mineralizations, but no distinct Pd-anomaly is found here. High factor loadings for Pd, Te and Cu as compared to those in Peräpohja have not been located in Koitelainen area. Palladium emerges as a separate factor.

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11.3

PGE EXPLORATION IN SWEDEN

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At the request of State Mining Property commission (NSG) Swedish Geological Co (SGAB) has since 1985 carried out an exploration project with special interest in Platinium-group elements (PGE).

From the late 60's until 1983 there was a Ni-exploration campaigne in Sweden. During the course of this campaigne anomalous PGE-values were registered in the newly found Ni-mineralizations. However, preliminary studies indicated mafic layered intrusions to be the only realistic targets for primary PGE-exploration in Sweden.

When the project started, only some 10 layered intrusions were known in Sweden. By now, a total of about 70 mafic layered intrusions have been recognized. The exploration has been concentrated mainly to Precambrian environments. Intrusions studied in detail are of three different ages, 1) about 2.45 Ga (Kukkola), 2) 1.85-1.9 Ga (Notträsk, Kläppsjö, Flinten), 3) 1.55 Ga (Nordingrå, Ragunda). Layering in the intrusions is often extremely well developed. The Kukkola intrusion close to the Swedish - Finnish border forms the north-westerly branch of the large early Proterozoic layered complex in northern Finland. Except for chromitite seams, up to 0.1 m in width the intrusion has disclosed Pt + Pd concentrations just under 2 ppm.

Anomalous PGE-Au concentrations have also been found in intrusions at Notträsk, Hoting, Kläppsjö and Flinten. As far as we know today they are all subeconomic.

Difficulties to reproduce analysis results and to find platinium group minerals (PGM) in polished sections indicate extreme nugget effects.

More detailed investigations of the identified mafic layered intrusions and the presumptive PGE-targets in Sweden continues.