Techniques and methodology used in a mineralogical and osmium isotope study of platinum group minerals from alluvial deposits in Colombia, California, Oregon and Alaska

I. C. LYON[1], H. TAMANA[1,2], D. J. VAUGHAN[1], A. J. CRIDDLE[2], J. M. SAXTON[1], AND P. VAN LIERDE[1,3,*]

[1]Department of Earth Sciences, The University of Manchester, Manchester, M13 9PL, UK
[2]Department of Mineralogy, The Natural History Museum, London, SW7 5BD, UK
[3]VG Isotech, Fisons Instruments, Aston Way, Middlewich, CW10 0HT, UK

Abstract

Platinum-group minerals (PGM) from placer deposits in Colombia, California, Oregon and Alaska were investigated with the electron microprobe, proton microprobe (μ-PIXE) and ion probe to analyse their major and trace element contents and $^{187}Os/^{186}Os$ isotopic ratios. Most of the grains in the samples investigated proved to be essentially homogeneous alloys of Pt-Fe and Os-Ir-Ru although a few of them contained inclusions of other PGM such as cooperite and laurite. Detailed analyses were undertaken on the Os–Ir–Ru alloy phases.

The $^{187}Os/^{186}Os$ isotope ratios fell into a range from 1.005 to 1.156 and are consistent with data published on PGM from other placer deposits from these regions. The ratios, together with the trace element data (and in particular the low rhenium content) determined by ion probe and μ-PIXE, indicate that crustal osmium was not incorporated in the grains and that no significant evolution of the $^{187}Os/^{186}Os$ ratios occurred during their history. These data, along with mineralogical and textural evidence, are consistent with a mantle origin for the grains through ultramafic intrusions, although the data do not entirely rule out alternative interpretations.

KEYWORDS: platinum group minerals, osmium isotopes, alluvial deposits, Colombia, Oregon, Alaska.

Introduction

AS part of a wider-ranging investigation of the mineralogy and geochemistry of platinum-group elements from eluvial and alluvial deposits (Tamana, 1994), a detailed study of osmium isotopes and trace elements in samples from alluvial deposits in Colombia, California, Oregon, and Alaska was undertaken.

The value of the ^{187}Re-^{187}Os decay system as a chronometer and as an isotopic tracer is now well established in geology and geochronology (e.g. Creaser *et al.*, 1991; Allègre and Luck, 1980; and Luck and Allègre, 1983). The basis of the technique is the strong fractionation of osmium into the mantle and rhenium (along with ^{187}Os, the daughter isotope of ^{187}Re) into the crust which implies that the $^{187}Os/^{186}Os$ of osmium in the crust has evolved over geological time to values of the order of 10–20 whilst $^{187}Os/^{186}Os$ values of osmium in the mantle are typically of the order of 1. Any material unaffected by crustal processes would be expected to show $^{187}Os/^{186}Os$ ratios close to bulk mantle values, currently accepted as being ~1.04 (Allègre and Luck, 1980); this represents an evolution from a ratio of 0.807, the calculated value for the Earth at 4.5Ga. The technique has been successfully applied to a range of problems, from the dating of meteorites (e.g. Luck and Allègre, 1983) and mantle xenoliths (e.g. Walker *et al.*, 1989), to the characterisation of the platinum group element (PGE) geochemistry of manganese nodules (Luck and Turekian, 1983; Luck, 1989). Application to understanding the origins of alluvial platinum-group minerals (PGM) is relatively recent. The present study adds new $^{187}Os/^{186}Os$ data for samples from Alaska, Oregon, California and

---

[*] Present address: Charles Evans Associates, 301 Chesapeake Drive, Redwood City, CA 94063, USA

Mineralogical Magazine, June 1997, Vol. 61, pp. 367–375
© *Copyright the Mineralogical Society*

Colombia to those already published (Hattori *et al.*, 1991*a,b*; Hattori and Cabri, 1992; and Hattori *et al.*, 1992) for placer grains from various locations around the world.

Sample localities and mineralogy

Most of the samples examined came from a collection made in the early 1940s by the late J.B. Mertie of mechanically concentrated and dredged placer-PGM from the western seaboard of North America. This collection is now housed in The Natural History Museum (NHM), London, with more recently acquired placer concentrates from Rio Pilpe, Colombia. All the samples from North America, including three groups of concentrates from Alaska, donated to the NHM by L.J. Cabri, are from the Cordilleran belt: five from California, three from Oregon, one from British Columbia and four from Alaska. Although the source rocks of these placer minerals are necessarily uncertain, it is probable that they came from ultramafic intrusions of the 'Alaskan' or 'Alpine' type. This is also true of the source rocks of the Colombian minerals, which were included in the current investigation because the tropical weathering environment from whence they came differs markedly from the environment of origin of the North American samples. For the latter, a random selection of the larger grain sizes were chosen from three localities: Snow Gulch, Arolik river, Alaska, (BM1982,321); Kubli Ranch, Applegate river, Jackson County, Oregon, (BM1982,318); and Burns Creek, Mariposa County, California, (BM1982,315). These are described below and further details are given in Tamana, 1994.

Snow Gulch, Arolik River, Alaska

Snow Gulch is a southerly trending ravine that drains into the Arolik River which flows into Kuskokwim Bay north of Goodnews Bay, Alaska. 2.14 grams of concentrates from Snow Gulch consist of grains varying in size from a small number (eight) of about 3 mm, down to several hundreds at the 1.0 mm, and thousands at each of the 0.5 mm and 0.25 mm size fractions. Most of the grains, which are a dull silvery grey, are rounded and appear to have been abraded. In all, 41 grains were separated, polished and analysed by electron microprobe. Many are monomineralic and homogeneous: about 40% are alloys of Pt and Fe, and 30% alloys of osmium, iridium and ruthenium, although the coarser fraction consists largely of Pt-Fe alloys of Pt_3Fe composition and the finer is dominated by alloys of osmium. Other monomineralic PGM grains include sperrylite, cooperite, irarsite and laurite. Gold is a minor constituent of the finer fractions. Three of the analysed osmium (Os–Ir–Ru alloy) grains were also analysed by μ-PIXE and by ion probe.

Kubli Ranch, Jackson County, Oregon

The Kubli Ranch sample came from a period of mining in 1941 from the mouth of Humbug creek at Applegate town upstream of the Applegate river.

The sample, weighing 3.16 grams, consists of a mixture of about 70% of PGM grains and 30% of silicates and oxides (mainly magnetic spinels). Very few grains are larger than 1 mm; the bulk (many thousands of grains) falling into 0.75, 0.5, 0.25 and $\leqslant$0.25 mm size fractions. The PGM are predominantly bright, silvery and untarnished, and most are flat and platey. Os–Ir–Ru and Pt–Fe alloys are dominant in the assemblage where they occur in the ratio 4:1. Of the 51 grains analysed by electron microprobe, more than 50% correspond compositionally to osmium (*sensu stricto*), 20% to isoferroplatinum and tetraferroplatinum, 16% to ruthenium and 10% to iridium. The remainder include grains of sperrylite, irarsite, laurite, ruarsite, gold and various PGE-bearing pentlandites. The isotopic ratios of four of the osmium grains were determined by ion probe.

Burns Creek, Mariposa County, California

The 6.21 grams of concentrates separated from the bench gravels of Burns Creek, sometime in 1941–42, are a by-product of dragline dredging for gold. Before the drainage pattern of Mariposa County was changed by damming, the major waterway that was Burns Creek (it is now a seasonal stream) drained a NW–SE trending strip of ultramafic rocks of Mesozoic age. These rocks are almost certainly the source of the PGM.

A small proportion of the concentrate (~10% by weight) exceeds 1 mm in grain size and consists predominantly of flat, round-edged grains of Pt–Fe alloys together with a few, mainly broken, crystals of osmium alloys, some florets or crystalline intergrowth of gold 'amalgam', and broken coils of tungsten lamp filaments (the latter two types probably being of artificial origin). About 65% of the concentrate is in the 0.5–1.0 mm size fraction, where, excluding the gold 'amalgam' and magnetic spinels, the PGM consist of between 93 and 98% Pt–Fe alloys and 2–5% Os–Ir–Ru alloys. The former, flat platey grains, with rounded edges, are so bright and silvery that they appear to have been 'sandblasted'. These anhedral grains contrast with the more steely blue colour of the subhedral to euhedral, unworn but often fragmentary, Os–Ir–Ru alloy grains.

Of the tens, if not hundreds of thousands of grains in this sample, 54 were selected at random for electron probe microanalysis. Most of them proved to be monomineralic: thirty-four were isoferroplatinum, one tetraferroplatinum, nine platinum *sensu lato*, five osmium, one iridium and one ruthenium, the others were grains of gold and gold 'amalgam'. Inclusions of other PGM were not abundant, but cooperite and idiomorphic inclusions of osmium were noted in some of the isoferroplatinum grains. Only one grain in the BM 1982,315 mount was observed to contain a significant abundance of osmium and this grain was analysed for osmium isotope ratios.

Rio Pilpe, Colombia

The Rio Pilpe river rises in the Cordillera Occidental mountains in the Cauca district of Colombia approximately 160 km south west of the city of Cali and becomes a tributary of the Rio Guapi. Twenty-one alluvial grains of PGM from this locality, all about 1 mm in size, were separated from a heavy mineral concentrate which included chromite, magnetite and various other spinels. These, and some gold, laurite and erlichmanite grains were mounted in epoxy resin and polished. The ratio of Os–Ir–Ru alloys to Pt–Fe alloys was approximately 10:1. Compositional data (and optical and X-ray data) for seven of the osmium-bearing grains in this polished mount (E.1318), including osmium (iridian), iridium, ruthenium and rutheniridosmine, are reported in Criddle and Stanley (1993). The osmium isotopic ratios for five of these grains were determined in this study.

Experimental methodology

The selected grains were analysed by electron probe microanalysis (EPMA) using a Cameca SX-50 electron probe (at The Natural History Museum, London) and by (micro) Proton Induced X-ray Emission (μ-PIXE) to ascertain bulk and trace element compositions. They were then analysed by ion probe (VG Isolab 54) at the Department of Earth Sciences, The University of Manchester, to measure osmium isotopic ratios and trace element abundances. Full details of these techniques are given below but the rationale of this approach was to use the electron probe to provide accurate bulk elemental abundances down to a detection limit of approximately 0.6 wt.%, in order that we could develop the technique of trace element analysis using the proton probe (which has an intrinsically lower detection limit than EPMA) and trace element analysis using the ion probe. The ion probe was then also used to measure ^{187}Os/^{186}Os isotope ratios for the grains. We report here the results of developing these two latter methods of trace element analysis for PGE, for although some elemental analyses of PGE have been acquired using the μ-PIXE technique (Criddle *et al.*, 1993), the technique required further development to yield accurate abundance measurements. Trace element analysis using ion probes is notoriously difficult to quantify accurately (Hinton, 1990), and the analyses given here are semi-quantitative.

Electron microprobe analyses

Electron probe microanalyses were obtained using a Cameca SX-50. The instrument was operated at a voltage of 20 kV and current of 25 nA. The following X-ray lines were used in the analyses: Sb-*L*α; S-*K*α; Fe-*K*α; Cu-*K*α; Ni-*K*α; Ru-*K*α; Rh-*K*α; Pd-*K*α; Ta-*K*α; W-*L*α; Re-*L*α; Os-*L*α; Ir-*L*α; Pt-*L*α; As-*K*α. Pure element standards were used for calibration in most cases (for the PGM) and particular care was taken to account for any peak overlap problems (Tamana, 1994).

μ-PIXE analysis

The μ-PIXE data were obtained using the Oxford University Scanning Proton Microscope (SPM); both the instrument and the analysis of platinum group minerals from placer deposits have been described elsewhere (Grime *et al.*, 1991; Criddle *et al.*, 1993).

Ion probe analysis

Osmium isotopic analyses and trace element analyses were obtained using a VG Isolab 54 ion microprobe which has been described in detail elsewhere (Lyon *et al.*, 1994; Saxton *et al.*, 1995; Saxton *et al.*, 1996). We followed methods described by Hattori *et al.* (1991*a*) and Hattori and Cabri (1992) for determining trace element and osmium isotope ratios, although we outline our method in some detail as we modified their procedures in order to improve the osmium ionisation efficiency and encountered some analytical difficulties which were not explicitly described in their papers.

Ion probe technique development — isotopic analysis

An $^{16}O^+$ primary ion beam from a duoplasmatron was used to sputter the metal grains. In the light of recent developments (eg. Creaser *et al.*, 1991) showing that Os easily forms an OsO_3^- ion during Negative Thermal Ionisation Mass Spectrometry (N-TIMS), we first studied the negative secondary ion spectrum in the hope that this would prove to be an efficient method of ionising Os by Secondary Ionisation Mass Spectrometry (SIMS). Unfortunately however, not only was OsO_3^- formed but also Os^-, OsO^-, OsO_2^-, and OsO_4^- and similarly, Re^-, ReO^-, ReO_2^-, ReO_3^-, and ReO_4^-. Also, combinations of each of these species with hydrogen and carbon yielded extremely complicated mass spectra which were difficult to interpret. Our hope had been that the ionization would be much 'cleaner' as in N-TIMS (Creaser *et al.*, 1991) allowing the natural speciation of osmium into OsO_3^-, and Re into ReO_4^-, which would allow the *in-situ* separation of the isobaric interferences ^{187}Os and ^{187}Re. However, the inherent ability of SIMS to form any molecular secondary ion (Eugster *et al.*, 1985), in abundances which may or may not bear any relationship to the stoichiometric composition of the sample under analysis, still holds true.

We thus reverted to the method of Hattori *et al.*, 1991*a* and Hattori and Cabri, 1992, in analysing positive secondary ions. An oxygen bleed was tried to improve the yield of Os^+ in an analogous manner to Walczyk *et al.*, 1991, and an improvement of up to a factor of 2 was obtained using a partial pressure of oxygen of 1×10^{-6} torr, although any higher partial pressure made the yield drop once again. All subsequent analyses reported below utilised these conditions and were obtained using peak switching of the osmium isotopes at a mass resolution of approximately 600 on an EPT electron multiplier. Low mass resolution was used in this investigation to increase the secondary ion current and facilitate the trace element analysis which required peak hopping between all masses from 20 u to 240 u. This did lead to problems of mass interferences described below, and in work subsequent to this paper we investigated the use of high mass resolution to overcome this problem (Bowles and Lyon, unpublished data).

The presence of other elements, particularly ruthenium, proved problematical; we found that Ru, with 7 stable isotopes and an extremely high ionization efficiency, often combined with other elements to fill the mass range with interferences at virtually every mass between masses 96 and at least 240 (the highest mass studied). Of particular concern were interferences which overlapped the mass values of osmium isotopes between masses 186 and 192. We identified one particularly troublesome interference as $RuFeO_2^+$, which formed interferences at all masses between 182 and 198. Figure 1 shows a mass spectrum which covers the mass range of the osmium isotopes displaying interferences at masses 183 and 184 where no single atomic ion should be observed. Osmium isotopic ratios acquired in this manner were usually anomalous, in some instances yielding $^{187}Os/^{186}Os$ ratios below present day mantle values due to the presence of a significant interference at mass 186. Our solution to this problem was to use energy filtering, a technique used elsewhere for removing molecular interferences (Benninghoven *et al.*, 1987*a*). This technique depends upon the fact that the yield of molecular ions usually drops much more rapidly as a function of increasing secondary ion energy than single atomic ions. Shown in Fig. 2 is the same region of the mass spectrum as in Fig. 1, but selecting only those ions with energies between 56 and 78 eV above the nominal ground potential of the sample. The interfering masses, for example the diagnostic masses at 183 and 184, were now absent. We were able to ascertain that the ruthenium interference problem had been reduced to insignificant levels by measuring the $^{186}Os/^{188}Os$ ratio which was found (when corrected for minor hydride interferences and mass fractionation as described below) to be within analytical error of the currently accepted $^{186}Os/^{188}Os$ ratio (Volkening *et al.*, 1991).

The energy filtering technique could not remove hydrides and rhenium interferences, however, and so small corrections were required to the measured isotopic ratios. Although EPMA indicated that the rhenium content of the grains was below the detection limit of the electron probe (<0.6 wt.%), a small peak was sometimes observed in the secondary ion spectrum at mass 185 (^{185}Re). We attribute the presence of this peak to the relatively efficient ionisation of rhenium which is much larger than the ionisation efficiency of osmium (Benninghoven *et*

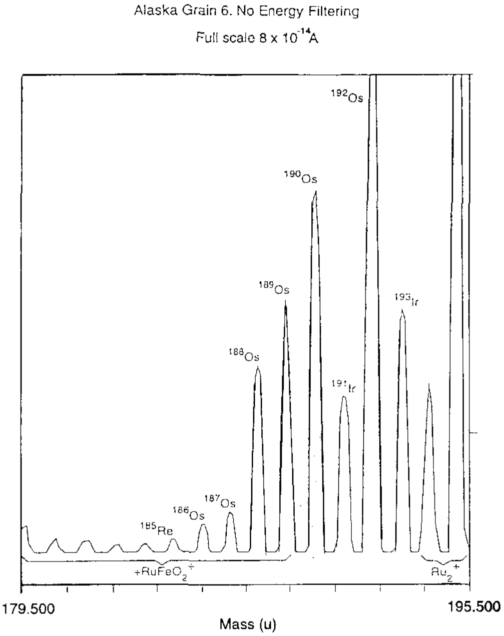

FIG. 1. A low mass resolution mass scan between masses 179.5 and 195.5 of osmium isotopes, but showing the presence of isobaric interferences such as $RuFeO_2$ and Ru_2^+.

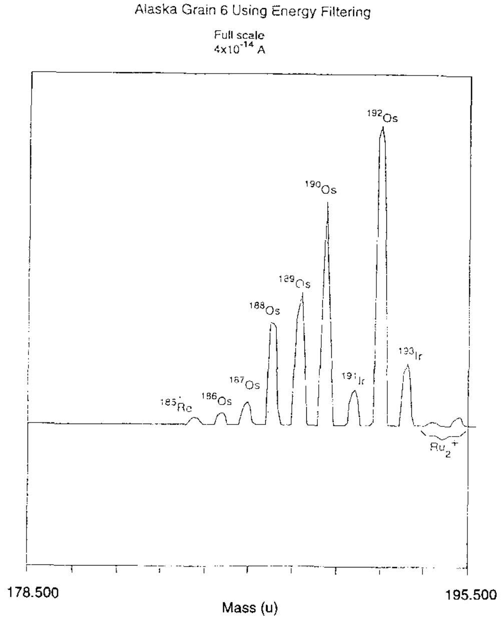

FIG. 2. An identical mass scan to Fig. 1 but using the technique of energy filtering to remove molecular interferences.

al., 1987*b*). There were also hydrides of osmium isotopes present which were not efficiently removed by energy filtering. Fortunately, we were able to use four abundant isotopes of osmium (^{186}Os, ^{188}Os, ^{189}Os, and ^{190}Os) whose relative abundances are known with high accuracy (Volkening *et al.*, 1991) to perform corrections for instrumental mass fractionation and hydride corrections. Iridium was also present at masses 191 and 193 which ruled out the use of the most abundant isotope ^{192}Os, as there was a correction at mass 192 from ^{191}IrH which was difficult to quantify. Isotope ratio measurements were obtained by measuring ion currents at masses 184.5 (background), 185, 186, 187, 188, 189 and 190. Data analysis software was written to solve a set of simultaneous equations using the known abundances of ^{186}Os, ^{188}Os, ^{189}Os, and ^{190}Os to yield the mass fractionation factor, the hydride contribution, the ^{185}Re/^{186}Os ratio and the ^{187}Os/^{186}Os ratio. It was necessary to assume that the hydride to atomic ion ratio (^{n}OsH/^{n}Os) was the same for all isotopes and the same for rhenium also. The determined mass fractionation factor was assumed to apply equally to rhenium and thus the ^{187}Re/^{186}Os ratio was calculated by using the known ^{187}Re/^{185}Re ratio. After correction of the measured mass187/mass186 ratio for ^{187}Re, hydrides and mass fractionation, the ^{187}Os/^{186}Os ratio was determined. ^{186}OsH and ^{187}Re corrections to the ^{187}Os peak height were typically no more than 3% and the measured mass fractionation was typically 5‰ u^{-1}.

Ion probe technique development—trace element analysis

Trace element analysis using ion probes has several advantages over many other analytical techniques which include high sensitivity, low background and *in-situ* analysis. It is, however, only semi-quantitative at present and quantitative trace element analysis is still evolving and subject to a number of limitations (Hinton, 1990). Total and relative ion yields of different elements can vary depending upon the precise operating conditions and chemical composition of the sample and hence the derived elemental abundances have a large error (which potentially can be up to a factor of 5 or more). This is because the ion yield for individual elements is highly dependent upon the sample chemistry, oxygen partial pressure, oxygen content of the surface and similar parameters which are difficult to quantify. One technique which may alleviate this problem is the use of relative sensitivity factors (RSF) (Cabri and McMahon, 1995) using implanted rare isotopes of elements that are desired for analysis. Unfortunately, this technique was not available to us at the time the measurements reported in this paper were obtained.

We obtained mass scans using the energy filtering technique described above to record the intensity of all secondary ions between masses 20 and 240. This technique ensured that the mass spectrum was relatively clean, consisting mainly of single atomic ions which in most cases could be unambiguously identified, usually from isotopic abundance patterns. In many cases we were able to identify the presence of elemental species below the detection limit of the electron probe or μ-PIXE. Using the measured relative peak heights and published tables of measured ionisation efficiencies (Benninghoven *et al.*, 1987*b*), we calculated the relative abundances of the detected elemental species, but the correlation between abundances measured by the electron probe and those by ion probe, even for bulk components such as individual PGE, was only semi-quantitative. In particular, ruthenium was usually over-estimated by up to a factor of two and osmium under-represented by up to a factor of two relative to their EPMA measured abundances. We cannot, with confidence, therefore define the abundance of trace elements such as Mg and Ti which were below the detection limit of both the electron microprobe and proton microprobe with an accuracy greater than a factor of two or three.

The main source of uncertainty in the measurements follows from a lack of appropriate ionisation efficiency factors for these elements sputtered from a PGE-rich matrix under conditions of high oxygen partial pressure. Total and relative ionisation efficiencies are notoriously variable for elements sputtered from different chemical matrices under varying conditions of oxygen partial pressure (Benninghoven *et al.*, 1987*b*) and the published values used here (*ibid.*) were obtained for positive ion yields obtained from (in most cases) pure metal samples of that element. We believe that these data are the closest approximation in the published literature to representative ion yields for positive ions sputtered from Os-Ir-Ru alloy grains. The calculated weight percentage compositions for the major elements usually agree to within a factor of two of the weight percentage compositions obtained by EPMA which is a reasonable level of agreement considering the uncertainties inherent in the method. Although semi-quantitative, the ion probe analyses are able to demonstrate the presence of some elements which are below the detection limits of EPMA and μ-PIXE.

The energy filtering technique removed many molecular interferences from the measured mass spectrum, but very intense interferences such as Ru_2^+ (which were still present at a significant level and produced peaks at masses between 192 and 208) meant that no reliable identification could be made of elements heavier than osmium. This was especially true of platinum, which was known to be present from EPMA analysis, but which has an extremely low ionisation efficiency during SIMS using an oxygen primary beam. Similarly, although energy filtering markedly reduced the level of molecular interferences, there were still some small peaks at many masses between 104 and 180 due to combinations of Ru with Fe, O, H and C which precluded the reliable detection of trace quantities of elements in this mass range. Fortuitously, interferences were reduced to insignificant levels between masses 180 and 192 when compared with the high-abundance osmium signal. However, in general, the presence of Ru in significant quantity in a sample proves a serious handicap to the determination of trace element abundances of elements heavier than mass 100.

Results and discussion

The $^{187}Os/^{186}Os$ isotope ratios for the measured grains are given in Table 1. They fall in the range 1.005 to 1.156 which is consistent with the data published on PGM from similar Alpine and Alaskan type intrusions (Hattori *et al.*, 1991*b*; Hattori and Cabri, 1992; Hattori *et al.*, 1992) although they are significantly different from the elevated $^{187}Os/^{186}Os$ ratios ($1.03 \leqslant {}^{187}Os/^{186}Os \leqslant 2.4$) measured from placer grains from the Freetown peninsula Sierra Leone (Hattori *et al.*, 1991*a*, Bowles and Lyon, unpublished data). The 'mantle like' ratios measured in grains from this study suggest that significant crustal osmium was not incorporated into the grains and that no significant evolution of the $^{187}Os/^{186}Os$ ratios took place during their history. The data are consistent with a mantle origin for these alluvial grains, their evolutionary history consisting of

TABLE 1. A compilation of measured $^{187}Os/^{186}Os$ ratios from Os–Ir–Ru alloy grains from the North American Cordillera and Colombia

Locality	Grain number	$^{187}Os/^{186}Os$	± error (1σ)
Rio Pilpe, Colombia	1	1.036	0.007
Rio Pilpe, Colombia	6	1.156	0.004
Rio Pilpe, Colombia	7	1.022	0.009
Rio Pilpe, Colombia	8	1.011	0.002
Rio Pilpe, Colombia	9	1.005	0.002
Burns Creek, California	BM 1982,315 3	1.050	0.006
Kubli Ranch, Oregon	BM 1982,318 D5	1.047	0.007
Kubli Ranch, Oregon	BM 1982,318 D8	1.075	0.007
Kubli Ranch, Oregon	BM 1982,318 D15	1.012	0.011
Kubli Ranch, Oregon	BM 1982,318 D16	1.027	0.004
Snow Gulch, Alaska	BM 1982,321 1	1.027	0.003
Snow Gulch, Alaska	BM 1982,321 2	1.007	0.006
Snow Gulch, Alaska	BM 1982,321 6	1.026	0.009

TABLE 2. Measured trace element abundances in selected Os–Ir–Ru alloy grains from the Arolik River, Alaska, to compare measured abundances from EPMA, μ-PIXE and ion probe. Ion probe measured abundances are semi-quantitative only and likely to be accurate to only a factor of two or three

	BM 1982 321C1				BM 1982 321C2				BM 1982 321C6		
Element	Ion probe	EPMA	PIXE	Element	Ion probe	EPMA	PIXE	Element	Ion probe	EPMA	PIXE
Mg	0.0	n.a.	0.00	Mg	0.01	n.a.	n.a.	Mg	0.02	n.a.	n.a.
Al	4.1E-04	n.a.	0.01	Al	0.07	n.a.	n.a.	Al	0.01	n.a.	n.a.
Si	7.9E-04	n.a.	0.01	Si	0.02	n.a.	n.a.	Si	0.01	n.a.	n.a.
K	0.0	n.a.	0.00	K	7.9E-03	n.a.	n.a.	K	0.02	n.a.	n.a.
Ca	0.0	n.a.	0.00	Ca	7.9E-03	n.a.	0.00	Ca	1.1E-03	n.a.	0.00
Ti	0.0	n.a.	0.00	Ti	0.03	n.a.	0.00	Ti	0.04	n.a.	0.00
V	3.7E-04	n.a.	2.00E-03	V	0.0	n.a.	n.a.	V	1.8E-03	n.a.	n.a.
Cr	2.2E-04	n.a.	1.00E-03	Cr	0.0	n.a.	n.a.	Cr	4.9E-04	n.a.	n.a.
Mn	0.0	n.a.	0.04	Mn	0.0	n.a.	0.00	Mn	3.1E-03	n.a.	0.06
Fe	*20.1	0.90	0.89	Fe	0.3	0.20	0.27	Fe	0.5	0.40	0.54
Ni	1.0	0.10	0.18	Ni	0.3	0.10	0.12	Ni	0.04	n.a	0.11
Cu	0.0	n.a.	0.12	Cu	0.0	0.00	0.11	Cu	0.0	0.00	0.00
Ru	14.4	21.40	22.20	Ru	53.5	29.90	37.39	Ru	56.3	38.90	45.42
Rh	1.8	1.90	1.97	Rh	0.5	0.50	0.40	Rh	2.1	0.70	0.85
Pd	0.0	n.a.	0.13	Pd	0.0	0.00	0.13	Pd	0.0	0.00	0.00
Sr	0.0	n.a.	n.a.	Sr	0.0	n.a.	n.a.	Sr	0.03	n.a.	n.a.
W	n.a.	n.a.	1.03	W	n.a.	n.a.	1.09	W	n.a.	n.a.	0.00
Re	4.0E-03	n.a.	1.67	Re	0.02	0.00	1.87	Re	0.09	0.00	2.02
Os	13.9	40.40	45.08	Os	14.6	41.50	48.12	Os	14.2	28.10	35.95
Ir	45.4	31.90	33.27	Ir	29.5	27.30	31.44	Ir	20.6	26.30	34.39
Pt	n.a.	4.50	5.07	Pt	n.a.	1.2	1.36	Pt	n.a.	6.00	7.14

*There is a very large difference between iron abundances measured by ion probe and EMPA and μ-PIXE for BM1982 321C1. It can only be supposed that the ion probe sputtered an iron rich inclusion which was not measured by the other techniques.

emplacement within ultramafic intrusions followed by weathering and transport, all without any measurable geochemical modification. Alternative explanations in which the PGE are mobilised through supergene or metamorphic processes, but where crustal contamination is minimal due to the relatively low levels of osmium in the host rocks are also possible, and cannot be completely ruled out by these data.

The trace element abundances (along with major element concentrations) in selected grains from Snow Gulch, Alaska, and from Kubli Ranch, Oregon, are given in Tables 2 and 3 respectively. Our previous work by μ-PIXE (Criddle *et al.*, 1993) suggested that in both bulk and trace element content, the grains analysed are essentially homogeneous; this observation is further confirmed here. The absolute values of trace element concentrations at the sub-microscopic level remain somewhat uncertain as the differences between the results of the two main methods of analysis (ion probe and μ-PIXE) show. However, a consistent overall pattern does emerge. In all of the analysed grains, in addition to the major elements Os, Ir and Ru and the minor elements detectable by EPMA (Pt, Ru, Fe, Ni) which are almost certainly present in solid solution in the Os–Ir–Ru alloys, a further fourteen elements have been detected by one or other of the analytical methods.

These elements fall essentially into one or other of three groups. The first are elements generally associated with the rock-forming silicate phases (Mg, Al, Si, K, Ca and Sr). Considering the occurrence of associated minerals as attached grains or rare inclusions (e.g. of olivine, pyroxene, biotite, plagioclase), these elements may result from sub-micron inclusions of these common minerals. The second group, of the first series transition metals Ti, V, Cr, Mn, Cu (which are in addition to the Fe and Ni noted above), may have been incorporated as trace elements in the alloy lattice or contained within such sub-micron included phases as chromite, ilmenite and bornite (which were among the larger inclusions noted in some samples). The remaining trace elements are W (found in only one grain analysed) and the other platinum group elements Pd and Re, all of which are likely to have been held in solid solution.

TABLE 3. Ion probe measured trace element abundances in two Os–Ir–Ru alloy grains from the Kubli Ranch, Oregon

BM 1982,318 D15		BM 1982,318 D16	
Element	wt.%	Element	wt.%
Mg	0	Mg	0.08
Al	0.009	Al	0.4
Si	0	Si	0
K	0.02	K	0.01
Ca	0.03	Ca	0.03
Ti	0	Ti	0
V	0	V	0
Cr	0.002	Cr	0
Mn	0.004	Mn	0
Sr	0	Sr	0
Fe	2.2	Fe	0.27
Ni	0.08	Ni	0.01
Ru	35.6	Ru	16.3
Rh	2.4	Rh	0.08
Os	19.4	Os	15.0
Ir	34.2	Ir	61.7
Re	0.008	Re	0

The suite of 'trace elements' found in these alluvial grains is that expected for PGE alloys derived directly from a magmatic, originally mantle, source. It can be explained, as noted above, by reference to associated (and possibly, included) major and accessory rock-forming minerals. The low rhenium content is also particularly significant, indicating that crustal osmium was not incorporated in the grains and that no significant evolution of the $^{187}Os/^{186}Os$ ratios occurred during their history. Thus, for these particular samples, both the data from osmium isotopes and from trace elements suggests that the grains are detrital and that they were released from the original host ultramafic rocks without significant chemical modification.

Acknowledgements

The major funding for the purchase of the Isolab 54 ion probe was made available by the University of Manchester out of its own and UFC funds and is gratefully acknowledged. Additional funding for capital items on the Isolab 54 has been made available by the Science and Engineering Research Council (now the Particle Physics and Astronomy Research Council) and the Natural Environment Research Council. PPARC also provided a research fellowship for J.M. Saxton. SERC support for the μ-PIXE probe at the University of Oxford is acknowledged and we thank Professor G. Grime for his assistance in the analysis of PGE using the Oxford PIXE probe. The Natural History Museum provided a research studentship for H. Tamana which is gratefully acknowledged. The authors are grateful to Fisons Instruments for the secondment of P. van Lierde to Manchester in order to assist in the development of this instrument and the techniques described. We also especially thank Mr D. Blagburn and Mr B. Clementson for their essential day to day support, maintenance and assistance with the Isolab ion probe and finally, but not least, to Professor G. Turner whose constant support and help has been invaluable in bringing the Isolab to its current state of usefulness.

References

Allègre, C.J. and Luck, J.-M. (1980) Osmium isotopes as petrogenetic and geological tracers. *Earth Planet. Sci. Lett.*, **48**, 148–54.

Benninghoven, A., Rudenauer, F.G. and Werner, H.W. (1987*a*) Secondary Ion Mass Spectrometry: Basic concepts, instrumental aspects, applications and trends. *Chemical Analysis*, Volume 86 (Elving, P.J. and Winefordner, J.D., Eds.), John Wiley and Sons, 987–90, and references therein.

Benninghoven, A., Rudenauer, F.G. and Werner, H.W. (1987*b*) Secondary Ion Mass Spectrometry: Basic concepts, instrumental aspects, applications and trends. *Chemical Analysis*, Volume 86 (Elving, P.J. and Winefordner, J.D., Eds.), John Wiley and Sons, 1102–5 (Table A7b).

Cabri, L. and McMahon, G. (1995) SIMS analysis of sulphide minerals for Pt and Au: Methodology and relative sensitivity factors (RSF). *Canad. Mineral.*, 349–59.

Creaser, R.A., Papanastassiou, D. and Wasserburg, G.J. (1991) Negative thermal ion mass spectrometry of osmium, rhenium and iridium. *Geochim. Cosmochim. Acta*, **55**, 397–401.

Criddle, A.J. and Stanley, C.J. (eds.) (1993) *The Quantitative Data File for Ore Minerals.* 3rd edition. Chapman and Hall, 699pp.

Criddle, A.J., Tamana, H., Spratt, J., Reeson, K., Vaughan, D.J. and Grime, G.W. (1993) Micro-PIXE analysis of platinum group minerals from placer deposits. *Nucl. Inst. Methods*, **B77**, 444–9.

Eugster, O., Armstrong, J.T. and Wasserburg, G.J. (1985) Identification of isobaric interferences. A computer program for ion microprobe mass spectral data. *Int. J. Mass Spec. Ion Proc.*, **66**, 291–312.

Grime, G.W., Dawson, M., Marsh, M.A., McArthur, I.C. and Watt, F. (1991) Oxford Scanning Proton Microprobe Facility. *Nucl. Inst. Methods*, **B54**, 52–60.

Hattori, K. and Cabri, L.J. (1992) Origin of platinum group mineral nuggets inferred from an osmium isotope study. *Canad. Mineral.*, **30**, 289–301.

Hattori, K., Cabri, L.J. and Hart, S.J. (1991*a*) Osmium isotope ratios of PGM nuggets associated with the Freetown layered complex, Sierra Leone, and their origin. *Contrib. Mineral. Petrol.*, **109**, 10–18.

Hattori, K., Cabri, L.J. and Hart, S.J. (1991*b*) Derivation of PGM nuggets from Alpine and Alaskan type intrusions confirmed by osmium isotope studies. *Abstract of the 6th International Platinum Symposium, Perth, Australia, August 1991*, I.A.G.O.D.

Hattori, K., Burgath, K.-P. and Hart, S.R. (1992) Os-isotope study of platinum-group minerals of chromitites in Alpine-type ultramafic intrusions and the associated placers in Borneo. *Mineral. Mag.*, **56**, 157–64.

Hinton, R.W. (1990) Ion microprobe trace-element analysis of silicates: measurement of multi-element glasses. *Chem. Geol.*, **83**, 11–25.

Luck, J.-M. (1989) Rhenium and osmium isotopes. *Nuclear Methods of Dating.* Chapter 4. (Roth, E. and Poty, B., Eds.), Kluwer Academic Press, Dordecht.

Luck, J.-M. and Allègre, C.J. (1983) ^{187}Re-^{187}Os systematics in meteorites and cosmochemical consequences. *Nature*, **302**, 130–2.

Luck, J.-M. and Turekian, K.K. (1983) ^{187}Os/^{186}Os in manganese nodules and the Cretaceous-Tertiary boundary. *Science*, **222**, 613–5.

Lyon, I.C., Saxton, J.M. and Turner G. (1994) Isotopic fractionation during secondary ionisation mass spectrometry. *Rapid Communications Mass Spectroscopy*, **8**, 837–43.

Saxton, J.M., Lyon, I.C. and Turner, G. (1995) High precision oxygen isotope ratio measurements obtained from geological and extra-terrestrial materials using an Isolab 54 ion microprobe. *The Analyst*, **120**, 1321–6.

Saxton, J.M., Lyon, I.C., Chatzitheodoridis, E., Perera, I.K., van Lierde, P., Freedman, P. and Turner, G. (1996) The Manchester Isolab 54 Ion Microprobe. *Int. J. Mass Spec. Ion Process.*, **154**, 99–131.

Tamana, H. (1994) *The mineralogy and geochemistry of platinum group minerals from eluvial and alluvial deposits.* PhD. thesis, The University of Manchester.

Volkening, J., Walczyk, T. and Heumann, K.G. (1991) Osmium isotope ratio determinations by negative thermal ionization mass spectrometry. *Int. J. Mass Spec. Ion Process.*, **105**, 147–59.

Walczyk, T., Hebeda, E.H. and Heumann, K.G. (1991) Osmium isotope ratio measurements by negative thermal ionization mass spectrometry (NTI-MS): Improvement in precision and enhancement in emission by introducing oxygen or freons into the ion source. *Fresenius J. Anal. Chem.*, **341**, 537–41.

Walker, R.J., Carlson, R.W., Shirey, S.B. and Boyd, F.R. (1989) Os, Sr, Nd and Pb systematics of southern African peridotite xenoliths; implications for the chemical evolution of subcontinental mantle. *Geochim. Cosmochim. Acta*, **53**, 1583–96.

[*Manuscript received 16 May 1996:*
revised 18 October 1996]