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OCCURRENCE OF UNKNOWN Ru–Os–Ir–Fe OXIDES IN THE CHROMITITES OF THE NURALI ULTRAMAFIC COMPLEX, SOUTHERN URALS, RUSSIA

GIORGIO GARUTI[1] AND FEDERICA ZACCARINI

Dipartimento di Scienze della Terra, Universitá di Modena, via S. Eufemia 19, I-41100 Modena, Italy

ROBERTO CABELLA

Dipartimento di Scienze della Terra, Universitá di Genova, viale Europa 26, I-16132 Genova, Italy

GERMAN FERSHTATER

Russian Academy of Sciences, Ural Branch, Ekaterinburg, Str. Pochtovy per 7, Ekaterinburg 620151, Russia

ABSTRACT

Unknown Fe-bearing Ru–Os–Ir minerals were discovered as inclusions (5–35 μm) in chromitites of the Nurali ultramafic complex, southern Urals, Russia. Low analytical totals and semiquantitative determination of oxygen by electron microprobe analysis suggest that the minerals probably are oxides. Chemical compositions indicate (Ru + Os + Ir)/(Fe + Ni + Cu) ranging from 5 to 1, and wide Ru–Os substitution at relatively low Ir contents. The minerals exhibit characteristic optical properties: yellowish gray color, strong bireflectance, and extremely high anisotropy, similar to that of graphite. Measured values of reflectance (R_1: 25–27%, R_2: 28–38%, at $\lambda = 548.3$ nm), and micro-indentation hardness (VHN 339–466) are significantly lower than those of known PGE alloys, sulfides, arsenides, and sulfarsenides in the system Ru–Os–Ir. The investigated compounds are potentially new mineral species, PGE-oxides having stoichiometries between XO_2 and X_2O_3, in which the PGE are probably tetravalent and Fe trivalent. An origin by desulfurization and further oxidation of pre-existing laurite – erlichmanite crystals can be postulated for the Fe-bearing Ru–Os–Ir oxides of Nurali.

Keywords: ruthenium, osmium, oxides, chromitite, platinum-group minerals, platinum-group elements, ultramafic complex, Nurali, Urals, Russia.

SOMMAIRE

Nous avons découvert un assemblage de minéraux de Ru–Os–Ir ferrifères sous forme d'inclusions (5–35 μm) dans des chromitites du massif ultramafique de Nurali, dans le sectur sud de la chaîne des Ourales, en Russie. Les faibles totaux des analyses chimiques et la seule possibilité d'établir la concentration de l'oxygène par analyse à la microsonde électronique de façon semiquantitative font penser que ces minéraux seraient des oxydes. Les compositions chimiques indiquent une rapport (Ru + Os + Ir)/(Fe + Ni + Cu) entre 5 et 1, avec une substitution Ru–Os importante à faible teneur en Ir. Ces minéraux font preuve des caractéristiques optiques suivantes: couleur gris jaunâtre, forte biréflectance, et anisotropie extrêmement élevée, comparable à celle du graphite. Les valeurs mesurées de réflectance (R_1: 25–27%, R_2: 28–38% à $\lambda = 548.3$ nm) et de dureté par micro-indentations (VHN 339–466) sont considérablement plus faibles que celles des composés connus des éléments du groupe du platine, par exemple les alliages, sulfures, arséniures et sulfarséniures du système Ru–Os–Ir. Ces composés pourraient bien être des nouvelles espèces minérales, des oxydes ayant une stoechiométrie entre XO_2 et X_2O_3, dans lesquels les éléments du groupe du platine seraient tétravalents, et le fer, trivalent. Une origine par perte de soufre et par oxydation avancée de cristaux de laurite – erlichmanite pourrait expliquer la présence d'oxydes ferrifères de Ru–Os–Ir à Nurali.

(Traduit par la Rédaction)

Mots-clés: ruthénium, osmium, oxydes, chromitite, éléments du groupe du platine, minéraux du groupe du platine, complexe ultramafique, Nurali, Ourales, Russie.

INTRODUCTION

Oxidized compounds of Ru–Os–Ir–Fe have been previously reported from chromitites of the Vourinos complex, Greece, by Garuti & Zaccarini (1995, 1997), although the authors could not establish if the minerals are in fact intergrowths of Ru-rich alloy with Fe-hydroxides (goethite, limonite) or true oxides of the platinum-group elements (PGE). In the course of mineralogical investigation of chromitites from the

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[1] *E-mail address*: garutig@unimo.it

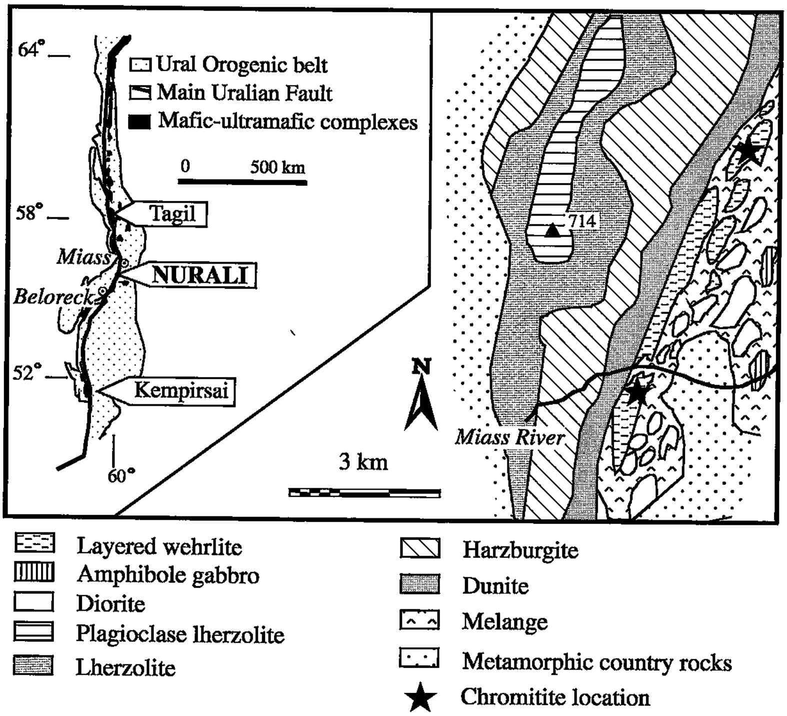


FIG. 1. Geographical location and geological sketch map of the Nurali mafic–ultramafic complex.

Nurali ultramafic complex in the southern Urals, Russia, compositionally similar platinum-group minerals (PGM) were systematically encountered within the altered portions of chromite crystals (Garuti *et al.* 1996). In this paper, we report the results of physical and chemical investigations of a number of grains from the Nurali occurrence, showing that the PGM are not mixtures of PGE alloy with Fe-hydroxides, but that they constitute single phases with specific optical and microhardness characteristics. The data available indicate that these PGM potentially represent new mineral species of PGE-oxides, although it was not possible to support this conclusion with a structural study because of the small size of the grains.

GEOLOGICAL SETTING AND OCCURRENCE

The Nurali ultramafic complex (Fig. 1) is located in the southern Urals, about 45 km southwest of Miass, and 65 km northeast of Beloreck. It is exposed along the Main Uralian Fault, and consists of a lower unit of mantle tectonite (plagioclase lherzolite, spinel lherzolite, harzburgite, and dunite) overlain by a layered pile of cumulates (dunite, wehrlite, clinopyroxenite, websterite), and upper amphibole gabbro and diorite. The complex has long been considered as a classic ophiolite sequence, although recents studies show that it may represent weakly depleted oceanic mantle (Savelieva 1987, Savelieva & Saveliev 1992) or, alternatively, lithospheric mantle below the continent–ocean transition zone (Garuti *et al.* 1997). Two bodies of chromitite a few square meters in size occur within the layered wehrlite. They are characterized by distinct assemblages of PGM, one consisting of laurite (RuS_2), erlichmanite (OsS_2), and Os–Ir alloy, the other dominated by Pt- and Pd-phases such as braggite (PtS), Pt–Fe alloy and undefined Pd sulfides (Smirnov & Moloshag 1994). The PGM grains generally appear as euhedral crystals included in fresh chromite, suggesting they are magmatic in origin, and that they were trapped in the chromite at a high temperature. The unknown oxygen-bearing Ru–Os–Ir–Fe minerals described in this paper do not pertain to this primary PGM assemblage. They typically occur in the rim of chromite crystals, in which Al and Mg are depleted, and Cr and Fe are enriched owing to alteration to ferrian chromite ("ferritchromit" of Spangenberg 1943). In addition, the PGM commonly are in contact with secondary silicates (serpentine, chlorite, zoisite, prehnite), possibly indicating an origin during some postmagmatic hydrothermal or metamorphic event.

ANALYTICAL METHODS

The oxygen-bearing Ru–Os–Ir–Fe mineral grains were initially located using reflected-light optical microscopy. They were subsequently investigated *in situ* by secondary electron microscopy (SEM), electron-microprobe analysis (EPMA) by both wavelength-dispersion (WDS) and energy-dispersion (EDS) modes, optical reflectance and microhardness.

The SEM images were obtained with a Philips 515 scanning electron microscope using an accelerating voltage of 20–30 kV, and a beam current of 2–10 nA. An ARL–SEMQ electron microprobe, equipped with EDS analyzer, was used for qualitative and quantitative analysis, being operated at an accelerating voltage of 25 kV and a beam current of 20 nA, with a beam diameter of about 1 μm. The following standards were used: pure metals, chromite, and synthetic NiAs, FeS_2, and $CuFeS_2$. The following X-ray lines were used: $K\alpha$ for S, Cr, Fe, Cu, and Ni, $L\alpha$ for Ir, Ru, Rh, Pt, Pd, and As, and $M\alpha$ for Os. Counting times were 10 s and 5 s for peak and background, respectively. On-line ZAF data-reduction and automatic correction for the interferences Ru–Rh, Ir–Cu, and Rh–Pd were performed using the PROBE software package (version 1996) by J. Donovan. The concentration of oxygen was determined in a separate run at 10 kV and 40–80 nA beam current, in order to improve the peak:background ratio. The $OK\alpha$ line was monitored for 30 s and 5 s counting time for peak and background, respectively, using a RAP crystal and flow-counter detector. Pure Cr_2O_3 was the reference material, allowing simultaneous analysis for Cr. Under these conditions, a minimum limit of detection of about 1.3 wt.% and a precision of ±10% were calculated from repeated analysis of the Cr_2O_3 standard. Strong fluctuation of the fluorescence signal was observed during the oxygen analysis of PGM grains, causing deterioration of both detection limit and precision, and resulting in semiquantitative determination of the concentration of oxygen.

Grain size was measured at 500× magnification using a Leitz micrometric ocular with a sensitivity of 0.1 μm, and expressed in square micrometers. Reflectance ($R\%$) was determined in air, with a Zeiss–Axioplan microscope equipped with microphotometer. Measurements were made with a 100 W tungsten source, a spot diameter of about 3 μm, and calibrated with a SiC standard ($R_{548} = 20.5\%$).

The Vickers hardness number (*VHN*) of the mineral could not be measured according to recommended standard conditions (minimum number of indentations = 10, applied load = 100 g, minimum time of lowering plus dwelling = 30 s), because of the small size of the grains. Microhardness was determined using 1) a Leitz Durimet instrument equipped with Vickers knob, applying the minimum load of 25 g for 30 s, and 2) a Futur–Tech Micro-hardness Tester FM–7 equipped with Knoop knob, enabling automatic conversion to the Vickers scale, operated at 10 g load and 5 s dwelling time. Knoop testing was preferred because the minor depth of indentation makes this method more efficient for small and thin specimens like those under investigation. In the range of microhardness investigated in this paper (*VHN* 300–900), the *KHN* and *VHN* values are approximately linearly correlated according to the equation: $y = 0.9658x - 6.86$. Only one indentation per grain was possible in most cases, and microhardness values were averaged from three readings, each one taken by a different operator.

RESULTS

Ore microscopy, reflectance and microhardness

The examination of 17 polished sections, representing about 8 cm² of surface, established the presence of 50 grains, with a maximum frequency of 15 grains in a single section; the Ru–Ir–Os–Fe minerals are by far most abundant in the Ru–Os–Ir-rich chromitite. The grains vary in shape from subrounded or irregular, to euhedral. They usually show a rugged surface and may contain cross-cutting vermicular veinlets of an Al–Mg silicate (chlorite?) in some cases arranged in radial symmetry. Under microscope observation in oil and tungsten-source illumination operated at about 3500 K, the grains are yellowish white, similar to millerite and heazlewoodite, and distinctly bireflectant from yellowish white to creamy or pinkish grey. The appearance of the unknown oxygen-bearing Ru–Os–Ir–Fe mineral under reflected light is shown in Figure 2A. Anisotropy is very strong, from bright grey to dark brown-gray, similar to that in graphite (Figs. 2B, C). Patchy extinction is common, varying from mosaic-like to radial-fibrous. A typical hourglass zonation has been observed in many grains, possibly due to twinning.

The minimum (R_1) and the maximum (R_2) values of reflectance were measured at wavelengths (λ) of 471.1, 548.3, 586.8, and 652.3 nm for the largest grain NU43–5, and have been plotted as spectral curves (Fig. 3). Further measurements at λ = 548.3 nm were obtained from four additional grains, in the range $26 < R_1 < 27\%$, $28 < R_2 < 38\%$.

Values of *VHN* were measured on twenty grains larger than 50 μm². Only in the case of one grain (NU43–5, 527 μm²) was it possible to obtain both Vickers and Knoop indentations. Indentation figures (Fig. 4) yielded quite similar values of hardness: $VHN_{25} = 464$, and $KHN_{10} = 492.3$, equivalent to $VHN = 468.6$. All other grains were tested only with the Knoop instrument, and the data converted automatically to the Vickers scale. Calculated *VHN* would appear to be strongly size-dependent (Fig. 5), reaching values higher than 600 in grains less than 100 μm². This dependence is due to the fact that indentation of small grains cuts into the surrounding chromite (*VHN* >1000), giving an apparent hardness higher than

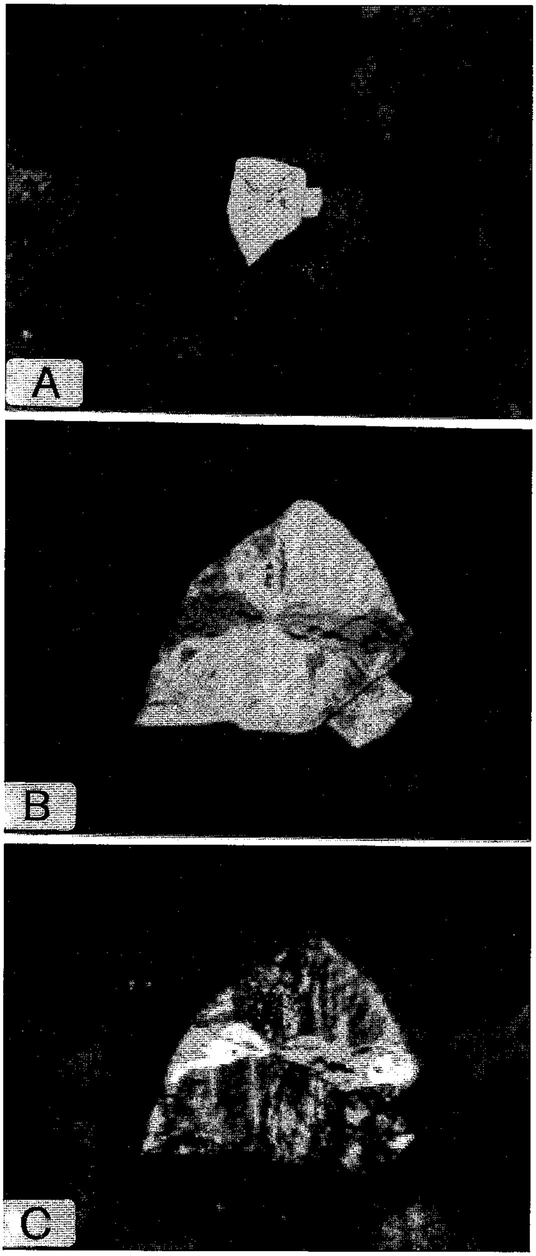
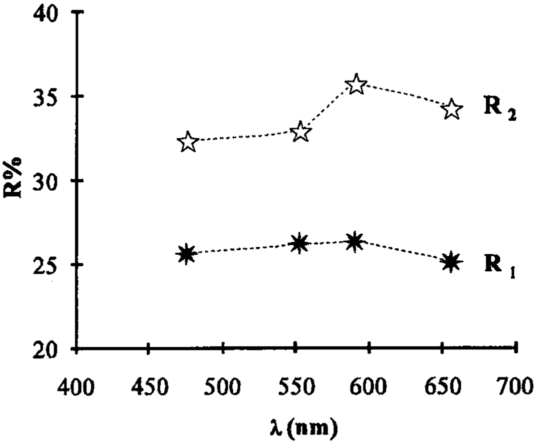


FIG. 2. Reflected-light (plane-polarized, oil immersion) images of grain NU43–5 (grain size: 32 × 21 µm). A. Parallel nicols, large-field image showing the textural position of the PGM grain. Medium grey: unaltered chromite with pitted alteration rims; black: Mg–Al silicate, probably chlorite. B and C. Images with crossed nicols showing the two maximum extinction positions at 90° and the distinct anisotropy. The altered chromite surrounding the PGM grain is characterized by strong internal reflections.



	Reflectance %	
λ (nm)	R_1	R_2
471.1	25.6	32.4
548.3	26.3	32.9
586.8	26.4	35.7
652.3	24.9	34.4

FIG. 3. Reflectance (%) measured in air, and spectral reflectance curves, for grain NU43–5.

expected. Surprisingly, a relatively high *VHN* of 668 was obtained from indentation of the 186 μm^2 grain (NU45–12) included in silicate (*VHN* = 80). A possible explanation is that the soft background of the grain probably yielded under pressure, resulting in a smaller indentation imprint, and thus apparent higher hardness. The data as a whole suggest that the true hardness of the PGE-oxide is probably close to, or even lower than, the average *VHN* value of 466.3 calculated for grain (NU43–5). The possible range of variation (339–466) is indicated in Figure 5.

The reflectance values (%R_{546}) in air (extrapolated from spectral curves) were plotted *versus* microhardness *VHN* (Fig. 6) in accordance with the experimental key-diagram of Tarkian & Bernhardt (1984). This diagram clearly shows that the investigated compounds are much less reflectant and softer than all the PGE alloys, sulfides, arsenides and sulfarsenides known in the natural system Ru–Os–Ir.

Electron-microprobe analysis

The results of the electron-microprobe analysis are presented in Table 1 as both element and oxide weight

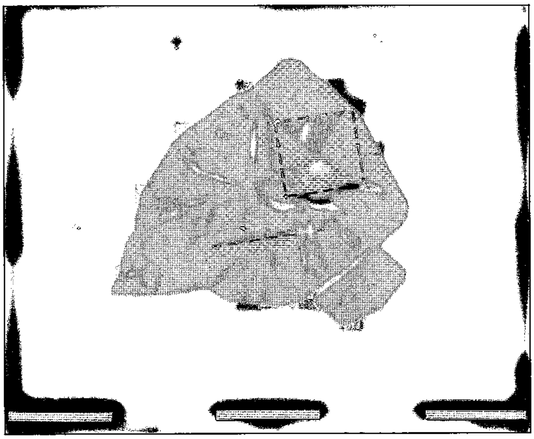


FIG. 4. SEM image of grain NU43–5 showing both indentation figures obtained by Vickers (square) and Knoop (cut) knobs. Scale bar: 10 µm.

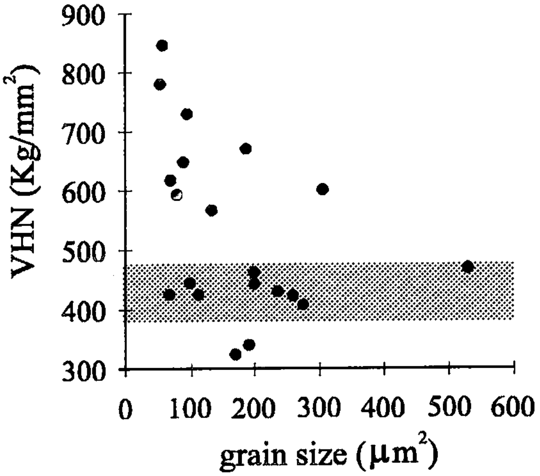


FIG. 5. Diagram showing dependence of calculated Vickers microhardness on size for 20 grains larger than 50 µm^2. The shaded area indicates the possible variation of true microhardness.

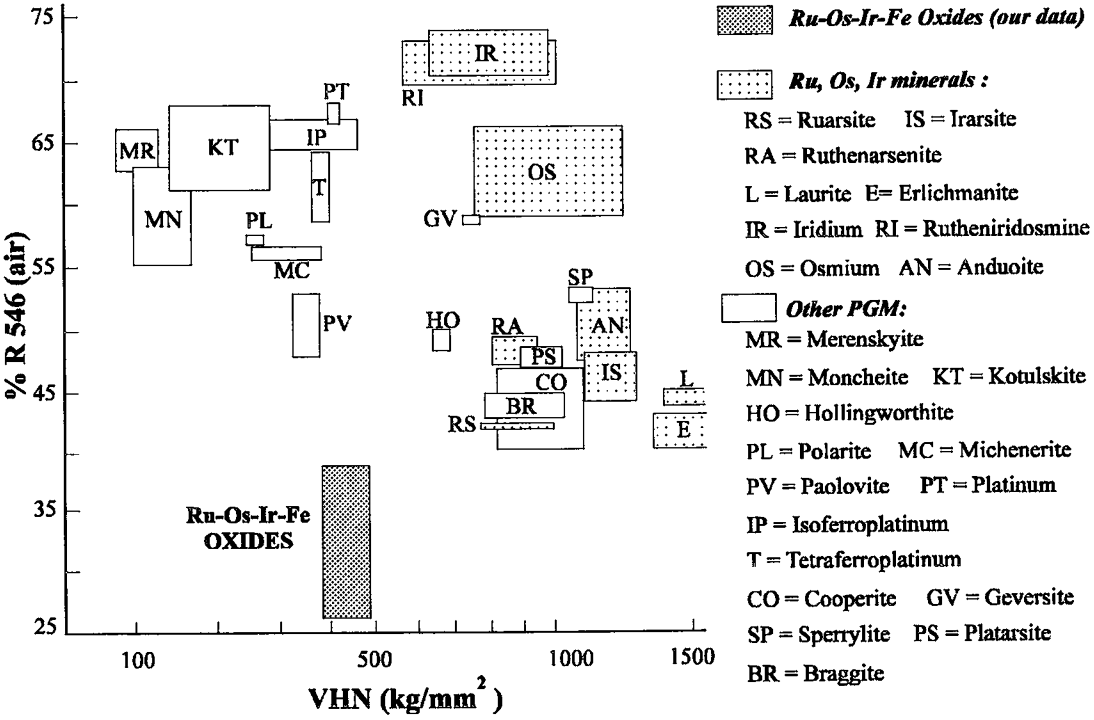


FIG. 6. Relationships between reflectance and microhardness for a number of PGM species. Redrawn after Tarkian & Bernhardt (1984). The Ru–Os–Ir–Fe oxide is less reflecting and softer than other PGM known to date in the Ru–Os–Ir system.

percentages. The metals Ru, Os, Ir and Fe are major constituents of the grains, along with minor Ni, Cr, Pd, and traces of Pt, Rh and Cu. The EDS spectra collected during the analysis of grains indicate that anions such as S, As, Te, Bi and Sb are conspicuously absent, although the group of elements Mg–Al–Si–(Ca) was observed in some grains, probably owing to excitation of the associated silicate material. The recorded contents of Cr are strongly size-dependent and dramatically increase in grains smaller than about 50 µm², confirming that the concentration of this element is related to spurious fluorescence from the chromite host. On the basis of this observation, the analyses were purged of all Cr, as well as of proportional amounts of Fe, calculated from the Cr:Fe ratio of the host chromite. Analytical totals are usually lower than 100 wt.% (typically around 80 wt.%), even in grains larger than 100 µm², and apparently free of pores or silicate inclusions. This shortfall was attributed to the probable presence of oxygen as an undetected light element. The oxygen content of the unknown Ru–Os–Ir–Fe mineral larger than 100 µm² was in the range 6–18 wt.%, and apparently independent of both grain size and Cr content. Following the reasoning of Garuti & Zaccarini (1997), we conclude that the detected oxygen is not due to fluorescence from the chromite host, but most probably is a major constituent of the PGM. Unfortunately, the low precision in the O determination makes the analytical results merely semiquantitative.

TABLE 1. SELECTED COMPOSITIONS* OF Ru–Os–Ir–Fe OXIDES FROM THE NURALI CHROMITITES

	NU43 5	NU43 7	NU43 8	NU44 10	NU44 13a	NU4425	NU44 28	NU46 1a	NU46 10	NU46 11	NU67 10
Element weight %											
Os	34.48	31.25	72.08	25.36	47.44	43.17	56.33	23.89	13.39	37.59	42.80
Ir	6.74	3.96	0.00	2.80	6.01	7.48	0.13	7.66	20.99	2.56	3.28
Ru	31.90	32.69	0.00	33.91	11.52	19.31	7.17	39.10	23.07	28.57	8.02
Rh	0.27	0.45	0.00	0.00	0.17	0.05	0.20	0.00	0.13	0.24	0.09
Pt	0.00	0.00	0.00	0.00	0.37	0.00	0.00	0.00	0.00	0.00	0.00
Pd	0.17	0.06	0.00	0.08	0.26	0.64	0.00	0.25	0.25	0.01	0.12
Fe	6.08	11.21	6.28	10.28	13.46	8.41	12.40	11.01	18.61	10.53	22.36
Ni	0.43	0.28	3.30	5.42	0.88	1.58	1.48	0.88	1.46	1.41	0.79
Cu	0.00	0.00	1.55	0.00	0.00	0.00	0.00	0.00	0.07	0.07	0.33
S	0.00	0.00	1.89	0.47	0.78	0.07	0.22	0.11	0.67	0.10	0.59
As	0.00	0.00	0.43	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.27
Total	80.07	79.89	85.52	78.31	80.88	80.70	77.93	82.89	78.64	81.07	78.63
Oxide weight %											
OsO_2	40.28	36.51	84.20	29.62	55.41	50.43	65.80	27.91	15.64	43.91	49.99
IrO_2	7.86	4.62	0.00	3.26	7.01	8.72	0.15	8.93	24.49	2.99	3.83
RuO_2	42.00	43.03	0.00	44.64	15.16	25.42	9.45	51.47	30.37	37.61	10.56
RhO_2	0.36	0.59	0.00	0.00	0.22	0.07	0.26	0.00	0.16	0.31	0.11
PtO_2	0.00	0.00	0.00	0.00	0.43	0.00	0.00	0.00	0.00	0.00	0.00
PdO_2	0.22	0.08	0.00	0.11	0.34	0.84	0.00	0.32	0.33	0.01	0.15
Fe_2O_3	8.69	16.02	8.97	14.69	19.25	12.02	17.73	15.74	26.61	15.06	31.96
NiO	0.55	0.35	4.20	6.89	1.11	2.02	1.88	1.12	1.85	1.80	1.01
CuO	0.00	0.00	1.94	0.00	0.00	0.00	0.00	0.00	0.09	0.09	0.41
Total	99.95	101.21	99.31	99.22	98.95	99.51	95.27	105.50	99.54	101.77	98.02

* Results of electron-microprobe analyses.

Weight percent metals were recalculated as ideal oxides, considering a constant valence of 4+ for PGE, 3+ for Fe, and 2+ for Ni and Cu. It is well known that the PGE may have a 2+, 3+ or 4+ valence state (Brookins 1987, Augé & Legendre 1994). A possible error in assuming the 4+ valence for Pt, Pd and Rh is practically insignificant owing to the concentration of these metals at trace levels in the analyzed grains. Among the other PGE whose concentration was determined, only Os is normally tetravalent, whereas both Ru and Ir may also occur with 3+ valence state in synthetic oxides. In spite of these uncertainties, recalculated results of analyses have totals close to 100 wt.% in most cases. Deviation toward lower values occur in grains smaller than 100 µm², or containing a substantial number of silicate inclusions, owing to the small excitation-volume (Garuti & Zaccarini 1997). Totals in excess of 100% were probably due to variation in the valence state of the PGE. Results indicate that the 4+ valence assumed for Os, Ru and Ir is the most likely valence state for the investigated compounds. Recalculated compositions in weight % oxides are shown in the (Ru + Os + Ir)–(Fe + Ni)–O diagram (Fig. 7A) and appear to vary between a stoichiometry of the rutile type, XO_2, and one of the hematite type, X_2O_3.

The distribution of metals generally exhibits (Ru + Os + Ir) > (Fe + Ni + Cu), with the ratio PGE : base metals varying from 5 to 1 atom %. Some grains contain substantial Ni, higher than Fe in some cases, whereas Cu is generally very low (Table 1). Compositional variations in the system Ru–Os–Ir (Fig. 7B) indicate that Ru is the dominant PGE in most grains, although there is a wide range of Ru–Os substitution at Ir contents generally lower than 10 atom %. However, it is interesting to note that Os predominates in some grains, and one is a pure osmium – base metals oxide (analysis NU43–8, Table 1). Some other grains, although dominated by Ru, contain substantial Ir (up to more than 20 at.%). These observations suggest the presence of more than one mineral species.

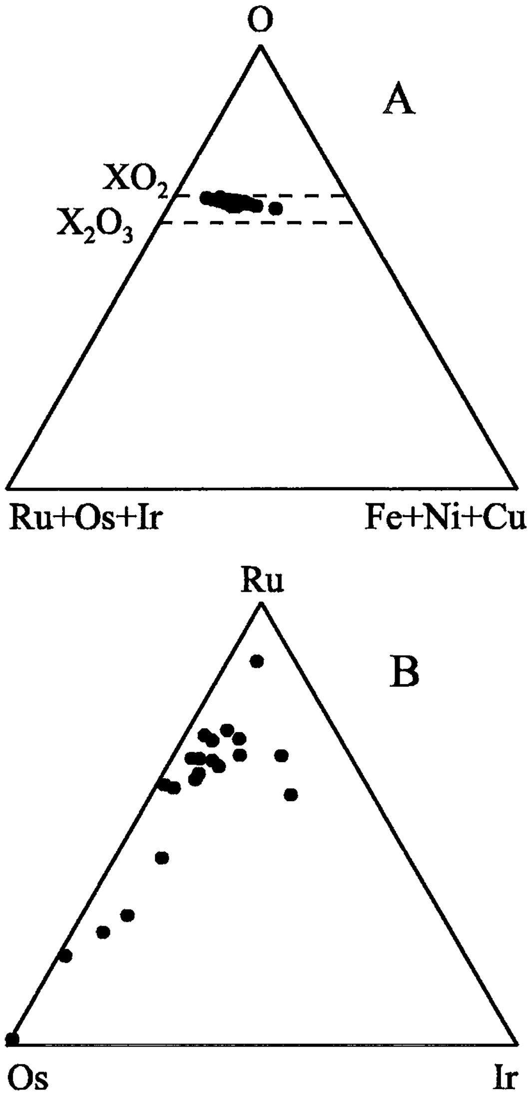


FIG. 7. A. Apparent stoichiometry after recalculation of the Ru–Os–Ir–Fe compositions as oxides (Table 1). B. Compositional variations (in atom %) in terms of the system Ru–Os–Ir.

DISCUSSION

The existence of natural oxides of the PGE is now well established, although in all cases of which we are aware, it was impossible to give a crystallographic characterization to the degree required for acceptance as new mineral species. This was generally due to the small size of grains, preventing any XRD-based structural study. On the basis of low analytical totals, relatively dark grey color on BSE images, the presence of oxygen in qualitative and quantitative electron-microprobe analyses, several types of oxides containing PGE as major constituents (Pt–Fe, Ir–Fe–Rh, Pt–Ir–Fe–Rh, Ru–Mn–Fe) have been reported from alluvial nuggets in a number of placer deposits of the world (Cabri *et al.* 1981, Nixon *et al.* 1990, Weiser 1991, Augé & Legendre 1992, 1994, Legendre & Augé 1992, 1993, Cabri *et al.* 1996). More recently, PGE oxides have been described *in situ*: Prichard *et al.* (1994) reported undetermined Pt and Pd oxides from serpentinized and weathered chromite-rich rocks of Shetland, and Augé & Legendre (1994) discovered Pt–Fe oxides in chromitites from the Pirogue ophiolite, New Caledonia, whereas Jedwab *et al.* (1993) and Olivo & Gauthier (1995) found PdO and (Pd,Cu)O in zones of hydrothermal alteration of the Itabira iron formation, Brazil.

Recently, Garuti & Zaccarini (1995, 1997) described oxygen-bearing Ru–Os–Ir–Fe compounds from weathered chromitites of the Vourinos complex, Greece. The authors suspected that these minerals could be Fe-rich Ru–Os–Ir oxides; however, they did not provide conclusive evidence for this inference, as in some examples, the minerals were found to be intergrown with goethite and limonite, suggesting the alternative possibility of mixtures of native PGE with Fe-hydroxides.

The oxygen-bearing Ru–Os–Ir–Fe minerals discovered in Nurali (Garuti *et al.* 1996) and described in this paper are similar in composition to those of Vourinos, but nowhere were they found intergrown with Fe-hydroxides. Detailed examination of some relatively large grains by SEM and optical microscopy reveals that they appear to consist of discrete phases, commonly showing a radially fibrous internal texture and twinning. Reflectance and microhardness properties indicate that the minerals are less reflectant and softer than any other PGM so far reported in the system Ru–Os–Ir. Recalculation of the metals sought (Ru, Os, Ir, Fe) as oxides yields analytical totals around 100 wt.% in many cases. On the basis of these observations, we suggest that the investigated PGM potentially represent new species of Fe-bearing Ru–Os–Ir oxides, in which the PGE have 4+, and Fe has 3+ valence. In the absence of XRD data, however, the existence of true PGE–O chemical bonding can only be postulated, as has been the case for other PGE oxides described to date.

The Nurali occurrence poses an interesting problem, concerning the origin and stability field of Ru–Os–Ir–Fe oxide in altered chromitites. In the Vourinos chromitites, the PGM coexist with abundant Fe hydroxides and ochres in a paragenetic assemblage typical of a gossan, and are believed to have formed during weathering by *in situ* desulfurization of primary crystals of laurite, the loss of S being compensated by gains in Fe, Ni, Cu, and O (Garuti & Zaccarini 1997). A similar origin by desulfurization and further oxidation of pre-existing laurite or erlichmanite crystals can be advanced for the grains of Nurali. Their composition displays the same variations in Ru–Os–Ir as natural laurite and erlichmanite. Furthermore, several grains were found to contain trace amounts of sulfur, possibly indicating incomplete desulfurization. In addition, the presence of radial fractures, commonly parallel to the fibrous structure of grains, suggests a volume reduction, as would be expected during any desulfurization process of sulfide minerals. However, at Nurali, weathering effects are absent, and chromite alteration appears to be unrelated to supergene conditions. The nature of secondary silicates in the chromitites rather support alteration during some postmagmatic hydrothermal or metamorphic event, which might have caused the postulated *in situ* desulfurization of primary laurite (Smirnov & Moloshag 1994). If the Ru–Os–Ir–Fe–O compounds from Nurali and Vourinos pertain to the same mineral species, the mineral would appear to be stable under a wide range of conditions, ranging from low-temperature supergene to relatively high-temperature hydrothermal. This possibility suggests that stabilization of this oxidized PGE-bearing phase is mainly controlled by variations in Eh rather than temperature.

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