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THE PGE AND BASE-METAL ALLOYS IN THE PODIFORM CHROMITITES OF THE LUOBUSA OPHIOLITE, SOUTHERN TIBET

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ABSTRACT

PGE and base-metal alloy minerals from podiform chromitites of the Luobusa ophiolite, southern Tibet include Os–Ir, Os–Ir–Ru, Pt–Fe, Ir–Ni–Fe, Fe–Ni–Cr, and Fe–Co with highly variable compositions. Small amounts of diamond, graphite, SiC, an unnamed chromium carbide, iron silicide (Fe–Si), and native Fe, Ni, Cr, Au, Cu and Si also are present. The alloys and native elements were recovered primarily from heavy-mineral separates of the chromitites, but some are included in, or attached to, magnesiochromite grains. They are mostly subhedral to anhedral and range in size from about 0.05 to 0.5 mm. Some grains have euhedral crystal forms and others have round shapes, suggestive of melt droplets. Fe–Ni-bearing, Ru-rich PGE alloys, Fe–Ni and Fe–Co alloys and native Fe and Ni in the Luobusa chromitites are interpreted as secondary minerals formed by alteration of PGE sulfides. The Pt–Fe, Os–Ir, and Ir–Ni–Fe alloys, Fe silicide and perhaps the native Si are considered to be xenocrysts from the mantle, transported to shallow depths by a rising plume and then captured by the melts from which the Luobusa chromitites crystallized.

Keywords: PGE minerals, base-metal alloys, chromitites, ophiolite, Luobusa, Tibet.

SOMMAIRE

Les lentilles de chromitite de l'ophiolite de Luobosa, dans le sud du Tibet, contiennent des minéraux du groupe du platine et des alliages de métaux de base, parmi lesquels figurent Os–Ir, Os–Ir–Ru, Pt–Fe, Ir–Ni–Fe, Fe–Ni–Cr, et Fe–Co, ayant une composition très variable. De plus, on a trouvé de petites quantités de diamant, graphite, SiC, un carbure de chrome sans nom, un siliciure de fer (Fe–Si), ainsi que Fe, Ni, Cr, Au, Cu et Si natifs. Les alliages et les éléments à leur état natif ont surtout été trouvés dans les concentrés de minéraux lourds présents dans les chromitites, mais dans certains cas, ils sont inclus dans ou rattachés à des grains de magnésiochromite. Ils sont en général sub-idiomorphes ou xénomorphes, et entre 0.05 et 0.5 mm de taille. Certains grains sont idiomorphes, et d'autres ont des formes arrondies, rappelant des gouttelettes de liquide. Les alliages riches en Ru et contenant du Fe et du Ni, ainsi que les alliages de Fe–Ni et de Fe–Co et le Fe et Ni natifs seraient des minéraux secondaires dus à l'altération de sulfures des éléments du groupe du platine. Les alliages Pt–Fe, Os–Ir, et Ir–Ni–Fe, le siliciure de fer et possiblement le silicium natif seraient des xénocristaux apportés du manteau dans une chambre à faible profondeur par un panache mantellique, pour ensuite être capté par des venues magmatiques, à partir desquelles les chromitites de Luobusa auraient cristallisé.

(Traduit par la Rédaction)

Mots-clés: minéraux du groupe du platine, alliages de métaux de base, chromitites, ophiolite, Luobusa, Tibet.

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INTRODUCTION

Natural metallic alloys have been reported from many localities and have been identified both in thin sections of ultramafic rocks (Stockman & Hlava 1984, Dmitrenko *et al*. 1985, Legendre & Augé 1986, Augé 1988, Rudashevsky *et al*. 1988, Melcher *et al*. 1997, Malich 1999) and in placers or soils spatially associated with ultramafic rocks (Cabri & Harris 1975, Bird & Bassett 1980, Nakagawa & Franco 1997). They are also commonly associated with chromian spinel in layered basic intrusions (Naldrett *et al*. 1987, Kinloch & Peyerl 1990), and generally fall into two compositional groups, one dominated by platinum-group elements (PGE), and the other, by base-metal elements (BM).

Most of the PGE alloys occur as primary inclusions in chromian spinel (*cf*. Stockman & Hlava 1984, Augé 1988, Melcher *et al*. 1997). Os–Ir, Os–Ir–Ru and Pt–Fe varieties, the most common, occur either as monophase minerals or composite grains associated with laurite (RuS_2), erlichmanite (OsS_2), silicates or PGE–BM sulfides (Augé 1988, Harris & Cabri 1991, Melcher *et al*. 1997). These primary inclusions are typically interpreted as early-crystallizing phases in chromian spinel (Stockman & Hlava 1984, Garuti & Zaccarini 1997, Melcher *et al.* 1997), either as pure alloys or PGE-bearing sulfides (Peck & Keays 1990). Some may also have formed from droplets of immiscible sulfide melt (Hulbert & von Gruenewaldt 1982).

Other PGE alloys and most BM alloys occur in serpentine or chlorite veins in podiform chromitites. They are usually polyphase minerals associated with sulfides or arsenides (Stockman & Hlava 1984, Corrivaux & Laflamme 1990, Melcher *et al*. 1997); their mode of occurrence suggests that they formed by relatively low-temperature alteration of PGE–BM sulfides (Stockman & Hlava 1984, Prichard & Tarkian 1988, McElduff & Stumpfl 1990, Nilsson 1990, Garuti & Zaccarini 1997). These intercumulus alloys may also be related to late-stage migration of silicate melts (Boudreau 1988) or hydrothermal fluids (Stumpfl & Rucklidge 1982).

The Luobusa ophiolite of Tibet contains a number of diamond-bearing podiform chromitites (Bai *et al*. 1993, Hu 1999) that shed considerable light on the magmatic and melt–rock reaction processes occurring in the upper mantle (Zhou *et al*. 1996). During an ongoing study of these rocks, we have discovered a variety of PGE and BM alloys, as well as native elements, from heavy-mineral fractions of the chromitites (Hu 1999). In this paper, we describe the assemblage of alloys and associated minerals, and discuss their paragenesis. We believe that the assemblage contains important information concerning the origin of primary PGE and PGE–BM alloys in chromitite deposits.

GEOLOGICAL SETTING

The Luobusa ophiolite is located on the south bank of the Yarlungzangbo River, about 200 km east-southeast of Lhasa (Fig. 1). It consists mainly of mantle peridotite and dunite overlying a *mélange* zone composed of pillow lavas, gabbros, pyroxenites and cherts in a serpentinite matrix. To the south, the ophiolite is separated from Triassic flysch by a steep reverse fault; to the north, it is thrust over the Tertiary Luobusa Formation and Gangdese granitic batholith. The ophiolite extends 42 km in an east–west direction and has an outcrop area of approximately 70 km^2.

Podiform chromitites occur discontinuously in a band in the upper mantle peridotites (Fig. 1). They display massive, disseminated, brecciated and nodular textures and consist of magnesiochromite with a relatively uniform composition [$74 < 100$ Cr/(Cr + Al) < 82]. On the basis of their composition and texture, the chromitites are believed to have formed by precipitation from boninitic melts interacting with the host peridotites (Zhou *et al.* 1996). These chromitites have an unusual mineral assemblage, including ultra-high pressure (UHP) minerals such as diamond and moissanite (SiC), as well as a number of highly reduced phases such as graphite, native chromium, iron, nickel, gold, copper and silicon identified by microprobe and X-ray diffraction studies (Hu 1999).

The Luobusa chromitites have relatively uniform chondrite-normalized PGE distributions, with enrichment in Os, Ir and Ru, and depletion in Rh, Pt and Pd, features typical of podiform chromitites (Zhou *et al*. 1996). The chromitites feature a wide range of Os (8.6–80.6 ppb), Ir (18.9–114 ppb) and Ru (114–212 ppb) concentrations and a relatively narrow range of Pt (0.41–3.24 ppb), Rh (5.02–10.4 ppb) and Pd (0.76–3.38 ppb) concentrations (Zhou *et al*. 1996). Variations in PGE abundance, chondrite-normalized patterns and Pd/Ir values have no apparent correlation with the distribution of the chromitite orebodies, their textural types, their bulk-rock compositions, or their chromium contents (Zhou *et al*. 1996).

SEPARATION PROCEDURES AND ANALYTICAL TECHNIQUES

In 1996, we collected a 1500-kg sample of chromitite from orebody 31 in the Luobusa ophiolite. In order to eliminate possible sources of contamination, the sample was removed directly from the orebody, carefully washed, air dried and crushed to pass a 1-cm sieve (for details, see Hu 1999). Mineral separation was carried out at the Institute of Multipurpose Utilization of Mineral Resources, Zhengzhou, China, using a combination of vibration, magnetic, flotation and electrical conductivity techniques. All of the equipment was carefully cleaned prior to processing, and a 200-kg granite sample was processed first as a blank to check for any contamination. This sample revealed only quartz, feldspar, garnet, mica, zircon and apatite.

The alloy minerals were hand-picked from several size-fractions, but most are between 0.1 and 0.3 mm in diameter. A few inclusions of Ir–Os and Os–Ir–Ru alloys were found within magnesiochromite grains

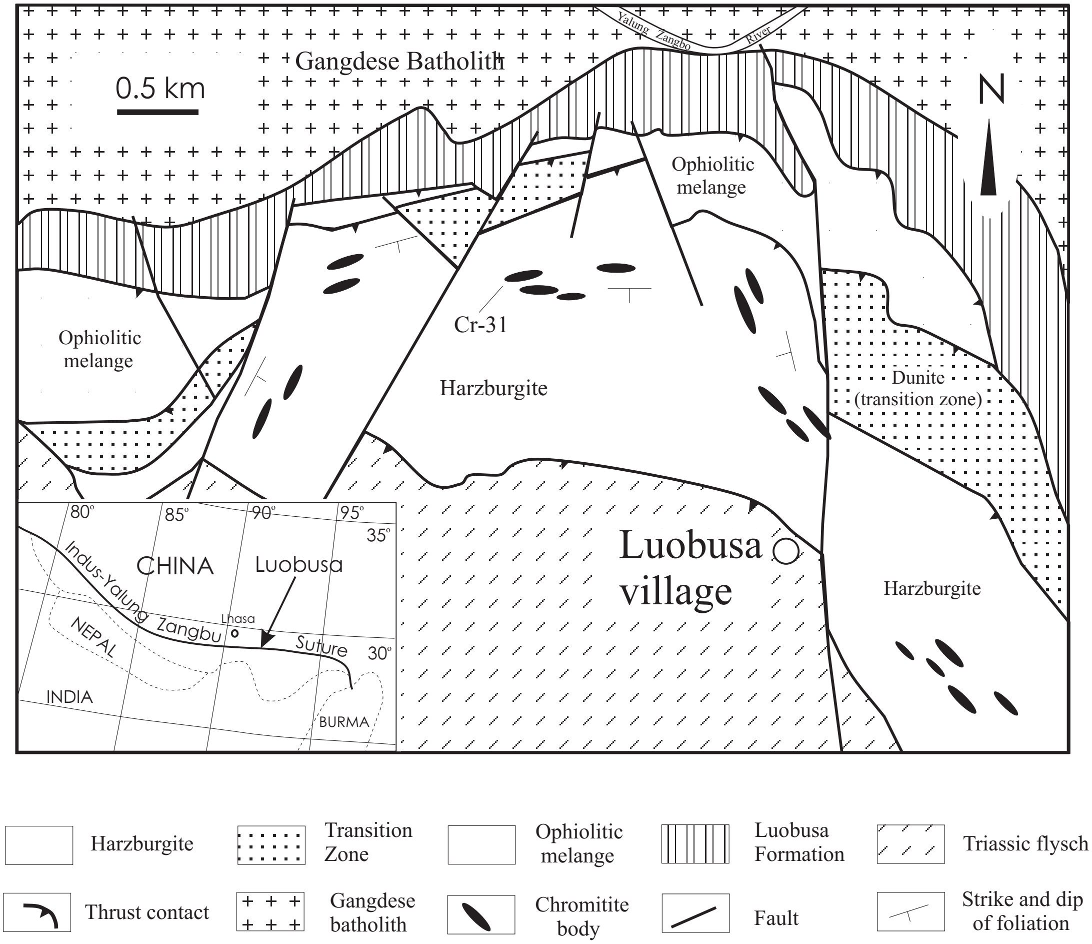

FIG. 1. Geological map of the Luobusa ophiolite showing the distribution of chromitite orebodies (after Zhou *et al.* 1996).

(Figs. 2A, B). The hand-picked grains were mounted in epoxy, machine polished, and analyzed with a SEM 505 scanning electron microscope equipped with a DEA 9100 energy-dispersion spectrometer at the General Research Institute of Mining and Metallurgy, Beijing, China. The optimum operating conditions for this equipment were: acceleration voltage 15 kV, beam current 12 nA, takeoff angle 35°, and counting times of 30–50 s. The Multi-Element Standard Program, SW9100 NOST, was used to analyze the spectra, and the results were checked using pure metal standards. The program normalizes all analytical results to 100%.

Alloy Minerals

Os–Ir and Os–Ir–Ru alloys

As in other chromitites, Os–Ir and Os–Ir–Ru alloys are the most abundant varieties in the Luobusa orebody. They typically occur as anhedral to subhedral, equidimensional grains, from 0.05 to 0.5 mm, as inclusions in magnesiochromite grains (Fig. 2A) or as individual crystals in the interstices between magnesiochromite grains (Fig. 2B). Some of the recovered grains are attached to magnesiochromite fragments, and some contain a Fe–Ni alloy as a separate phase. Others contain small inclusions of silicate or exsolution lamellae of Fe–Ir and Fe–Pt alloys.

The Luobusa Os–Ir and Os–Ir–Ru alloys span a wide range of compositions (Fig. 3) and are classified as osmium, iridium and ruthenium on the basis of the IMA-sanctioned system of nomenclature (Harris & Cabri 1991). Most of the grains of osmium and iridium alloys contain less than 10 at.% Ru and have a compositional range similar to those included in the Kempirsai chromitites of Kazakhstan (Melcher *et al*. 1997). A few grains contain up to 67 at.% Ru. A number of the osmium alloy grains plot in the experimentally determined

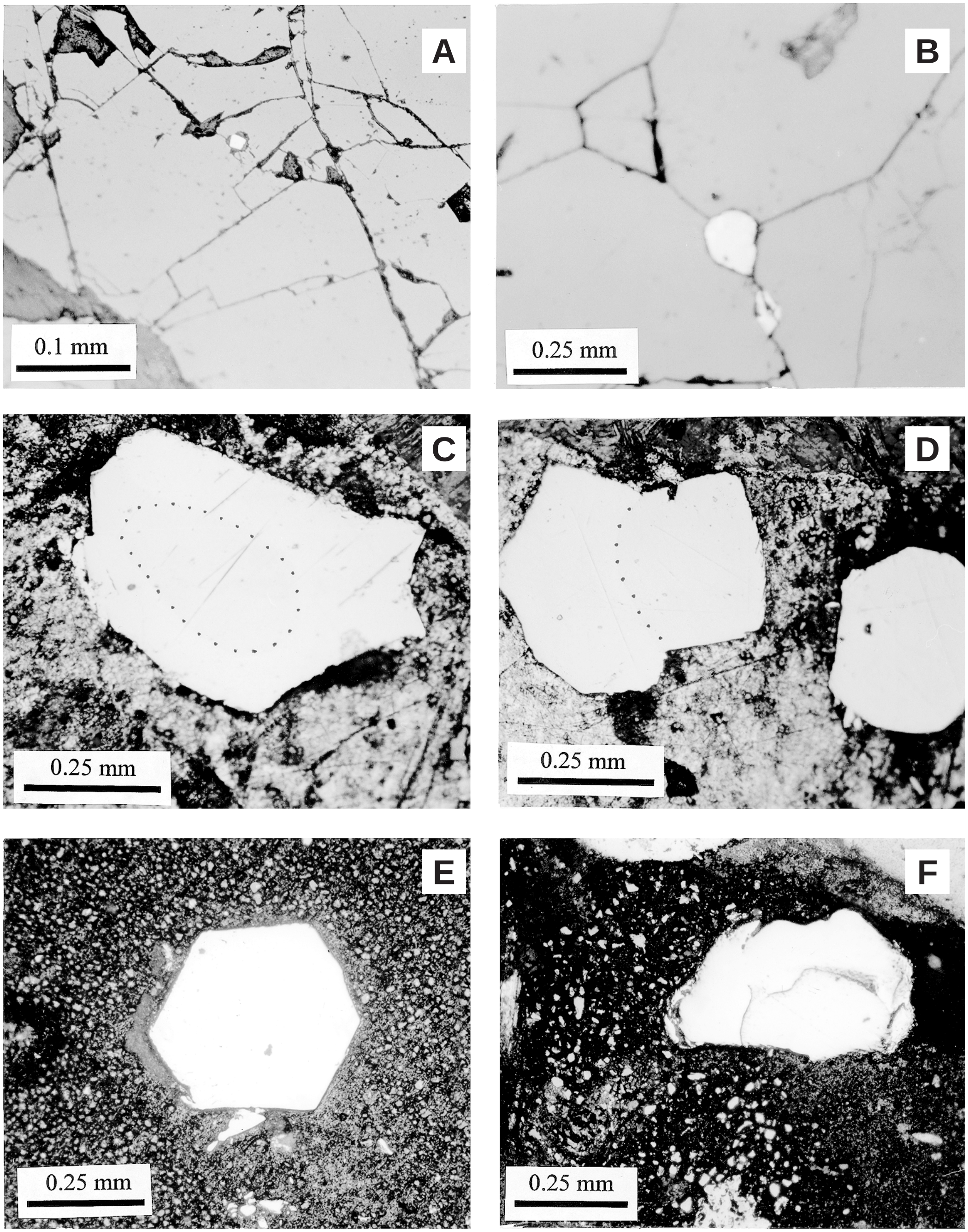

FIG. 2. Reflected-light photomicrographs of alloys from the Luobusa chromitites: A. Euhedral Os–Ir alloy completely enclosed in a magnesiochromite grain (sample B–1). B. Subhedral to anhedral grains of Ru–Os–Ir alloy along the boundary between magnesiochromite grains (sample 3100). C. Zoned Ir–Os alloy grain. Ovoid core is osmium ($Os_{0.59}Ir_{0.41}$), whereas the rim is iridium ($Ir_{0.67}Os_{0.38}$). Note the slight difference in color between core and rim (Sample 1–26). D. Large grain on the left is composite, with a “core” of iridium ($Ir_{0.66}Os_{0.34}$) and a rim of osmium ($Os_{0.57}Ir_{0.43}$). Note the sharp, curved boundary (emphasized) between the zones. The subrounded grain on the right is uniform osmium with the same composition as the rim (sample 024). E. Hexagonal crystal of Ru-rich Os–Ir–Ru alloy (sample 38–5). F. Zoned crystal with a core of $(Pt,Rh)_{0.70}(Fe,Ni)_{0.30}$ and a rim of Ru-rich Ru–Os–Ir alloy (sample 23–53). The matrix in C, D, E and F is epoxy.

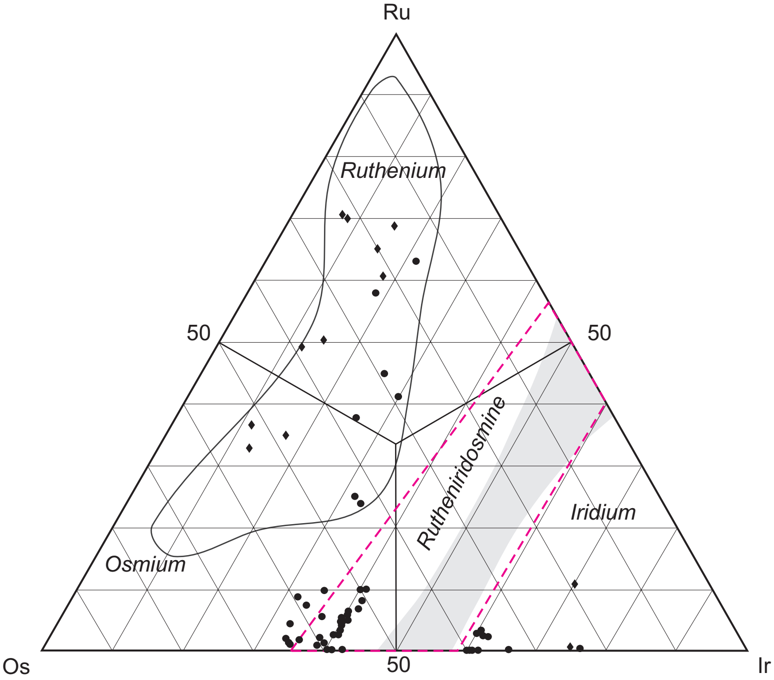

FIG. 3. Triangular diagram showing compositional variation of Os–Ir–Ru alloys in the Luobusa chromitites. Dots represent compositions of Os–Ir–Ru alloys, and diamonds represent compositions of BM-bearing Os–Ir–Ru alloys. The nomenclature and miscibility gap (shaded) are from Harris & Cabri (1991). The dashed lines show the boundaries of the experimentally determined 1-bar miscibility gap (Bird & Bassett 1980). The outlined field represents compositions of laurite and erlichmanite from Kempirsai, southwestern Oregon, and Samar in the Philippines and of porous Ru-rich Os–Ir–Ru alloys from the Oregon chromitites (data from Nakagawa & Franco 1997, Melcher *et al*. 1997 and Stockman & Hlava 1984).

1-bar miscibility gap of Bird & Bassett (1980), but lie outside the gap defined by natural occurrences Harris & Cabri (1991) (Fig. 3).

Osmium and iridium are commonly intimately intergrown, typically with cores of osmium and rims of iridium (Figs. 2C, D). The osmium cores have a slightly greyish cast in reflected light, and have a round or ovoid form. The iridium rims are white in reflected light and subhedral in outline (Figs. 2C, D). Os:Ir ratios in these alloys range widely from approximately 2:1 to 1:3, but the Os-rich varieties are most common (Table 1, Fig. 3).

Ruthenium is less common than either osmium or iridium, and typically occurs as subrounded grains between magnesiochromite crystals (Fig. 2B) or as euhedral hexagonal crystals, up to 0.4 mm across (Fig. 2E). These are homogeneous grains, ranging from about 37 to 67 at.% ruthenium (Table 1, Fig. 3). Compositionally, they grade into Ru-rich osmium, quite distinct from the more abundant Os–Ir alloy (Fig. 3).

Varied amounts of Fe, Ni and Cr were detected in some PGE grains, with maximum contents of 14.3, 17.0 and 1.5 at.%, respectively (Table 1). These PGE–BM alloys are mostly osmium and ruthenium (Fig. 3), with PGE:BM ratios ranging from 98 to 54.2. Some of them are compositionally similar to the Os–Ru–Cu–Fe alloy in Kempirsai, which was interpreted as due to secondary alteration (Melcher *et al.* 1997).

Pt–Fe alloy

Pt–Fe alloy occurs either as single grains, 0.1–0.4 mm across, or as intergrowths with, or exsolution-induced blebs in, Os–Ir–Ru alloy. Grains of the Pt–Fe alloy may be subrounded (Fig. 2F) or tabular in form (Fig. 4A). The tabular grain in Figure 4A is complexly intergrown with osmium, suggesting replacement of the Pt–Fe alloy along grain boundaries and cracks. In a few cases, the grains of Pt–Fe alloy contain small inclusions of Os–Ir–Ru alloy and RuS_2.

Most of these grains consist chiefly of Pt (52 to 72 at.%) and Fe (17 to 29 at.%), accompanied by varying amounts of Rh, up to 10.5 at.% (Table 2, Fig. 5). Ni,

TABLE 1. REPRESENTATIVE COMPOSITIONS OF Os-Ir AND Os-Ir-Ru ALLOYS FROM THE LUOBUSA CHROMITITES

Sample	3100	23-53	38-5	23-129	B-1	8-6	31-1-1	5-11	35-4-3	5-28	31-12-1	5-7A	1-18A
Os wt.%	31.85	33.24	36.08	43.53	48.38	20.15	57.92	51.51	60.07	53.50	62.92	56.43	39.78
Ir	11.26	24.34	33.87	32.34	36.47	73.07	36.50	43.58	35.91	43.35	34.39	41.99	60.23
Ru	54.72	42.43	30.04	24.14	15.13	6.17	5.58	4.90	4.02	3.15	2.70	1.58	0.00
Fe	1.46	0.00	0.00	0.00	0.00	0.61	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.71	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	100.00	100.01	99.99	100.01	99.98	100.00	100.00	99.99	100.00	100.00	100.01	100.00	100.01
Os at.%	20.78	24.23	28.61	35.99	42.84	18.98	55.41	49.60	58.23	52.29	61.67	55.90	40.03
Ir	7.27	17.56	26.57	26.46	31.95	68.12	34.55	41.52	34.44	41.92	33.35	41.16	59.97
Ru	67.20	58.21	44.82	37.56	25.21	10.94	10.05	8.88	7.33	5.79	4.98	2.95	0.00
Fe	3.24	0.00	0.00	0.00	0.00	1.96	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	1.50	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Sample	13-22	27-1-1	31-7-2	42-23	31-2	25-2-7	7-9	024c	024r	1-26c	1-26r	1-18-B	1-23
Os wt.%	36.90	35.21	64.59	59.48	63.22	61.18	23.47	33.37	57.10	59.00	37.77	59.00	37.46
Ir	61.57	63.26	33.93	39.26	35.92	38.26	76.21	66.63	42.91	41.00	62.23	41.00	62.54
Ru	1.53	1.53	1.48	1.26	0.85	0.57	0.32	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	100.00	100.00	100.00	100.00	99.99	100.01	100.00	100.00	100.01	100.00	100.00	100.00	100.00
Os at.%	36.64	34.97	63.98	59.07	62.99	61.11	23.59	33.61	57.35	59.26	38.02	59.26	37.71
Ir	60.50	62.17	33.26	38.58	35.41	37.82	75.80	66.39	42.65	40.74	61.98	40.74	62.29
Ru	2.86	2.86	2.76	2.35	1.59	1.07	0.61	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Approximate formulas: 3100: $Ru_{0.67}Os_{0.21}Ir_{0.07}$; 23-53: $Ru_{0.58}Os_{0.24}Ir_{0.18}$; 38-5: $Ru_{0.44}Os_{0.29}Ir_{0.27}$; 23-129: $Ru_{0.38}Os_{0.36}Ir_{0.26}$; B-1: $Os_{0.43}Ir_{0.32}Ru_{0.25}$; 8-6: $Ir_{0.70}Os_{0.19}Ru_{0.11}$; 31-1-1: $Os_{0.55}Ir_{0.35}Ru_{0.10}$; 5-11: $Os_{0.50}Ir_{0.41}Ru_{0.09}$; 35-4-3: $Os_{0.58}Ir_{0.35}Ru_{0.07}$; 5-28: $Os_{0.52}Ir_{0.42}Ru_{0.06}$; 31-12-1: $Os_{0.62}Ir_{0.33}Ru_{0.05}$; 5-7A: $Os_{0.56}Ir_{0.41}Ru_{0.03}$; 1-18A: $Ir_{0.60}Os_{0.40}$; 13-22: $Ir_{0.60}Os_{0.17}Ru_{0.03}$; 27-1-1: $Ir_{0.62}Os_{0.35}Ru_{0.03}$; 31-7-2: $Os_{0.64}Ir_{0.33}Ru_{0.03}$; 42-23: $Os_{0.59}Ir_{0.39}Ru_{0.02}$; 31-3: $Os_{0.63}Ir_{0.35}Ru_{0.02}$; 25-2-7: $Os_{0.61}Ir_{0.38}Ru_{0.01}$; 7-9: $Ir_{0.76}Os_{0.23}Ru_{0.01}$; 024c: $Ir_{0.66}Os_{0.34}$; 024r: $Os_{0.57}Ir_{0.43}$; 1-26c: $Os_{0.59}Ir_{0.41}$; 1-26r: $Ir_{0.62}Os_{0.38}$; 1-18-B: $Os_{0.59}Ir_{0.41}$; 1-23: $Ir_{0.62}Os_{0.38}$.

Co and Cu also were detected in a few grains, with maximum concentrations of 6.70, 4.23 and 18.73 at.%, respectively. One Pt–Fe grain contains 10.55 wt% Os (Table 2).

Only one of the analyzed grains of Pt–Fe alloy has a composition close to that of isoferroplatinum (Pt_3Fe), assuming that the deficiency in Pt is balanced by the incorporation of Rh, *i.e.*, $(Pt,Rh)_{0.74}Fe_{0.26}$ (sample 21–1, Table 2). Most of the other grains have an even higher proportion of (Fe + Ni + Co). The grain with 10.55 wt% Os has a formula of approximately $Pt_{0.64}(Rh,Os)_{0.19}Fe_{0.17}$.

Grains of Pt–Fe alloy with a similar composition but with up to 9.8% Pd, 3.9% Ir and 9.0% Rh, respectively have been reported from the New Caledonia ultramafic complex (Augé & Maurizot 1995). Pt–Fe alloy has also been reported from eastern Samar, Philippines, but detailed compositions are not given (Nakagawa & Franco 1997). Stockman & Hlava (1984) reported a Pt-rich alloy with 33% Fe from chromitite in southwestern Oregon. This alloy is associated with radial cracks in the chromian spinel, suggesting a formation similar to that of Ni–Fe alloy, by reduction of sulfides (*cf.* Dick 1974).

Isoferroplatinum (Pt_3Fe), platinian awaruite $(Ni,Pt)_3Fe$, and a series of complex Pt–Pd–Cu–Fe and Cu–Ni–Fe–Pt–Pd alloys were found in serpentine and magnetite in chromitites of Thetford Mines, Quebec and were interpreted to have formed by alteration of primary phases (Corrivaux & Laflamme 1990).

In summary, most of the Pt–Fe alloy at Luobusa does not fit an isoferroplatinum stoichiometry and contains little or no Pd, Ir and Rh. Thus, it is compositionally distinct from that reported in New Caledonia and Thetford Mines. However, many of these alloys may have been modified, at least in part, by subsolidus reactions or exsolution (or both) (*e.g.*, Bowles 1990).

Ir–Ni–Fe alloy

Ir–Ni–Fe alloy occurs as single grains up to 0.2 mm across (Fig. 4B) or as colloform intergrowths with

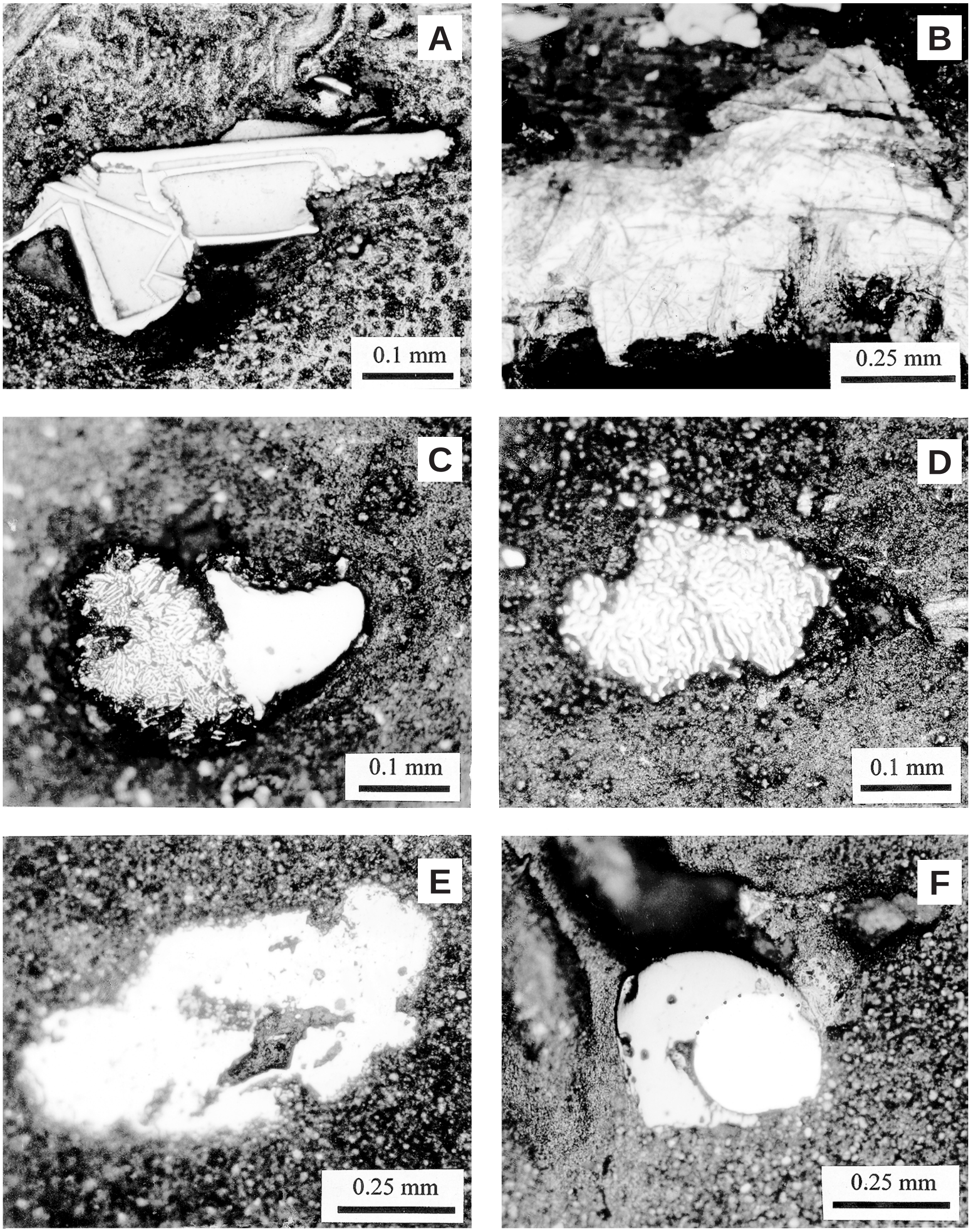

FIG. 4. Reflected-light photomicrographs of alloys from the Luobusa chromitites. **A.** Zoned tabular crystal with a core of Pt–Fe alloy $[(Pt,Rh)_{0.55}(Fe,Cu,Ni)_{0.45}]$ and a rim of osmium $(Os_{0.59}Ir_{0.39}Ru_{0.02})$ (sample 42–23). **B.** Irregular grain composed of awaruite (Ni_3Fe) (white) and Fe–Ni–Ir alloy (yellowish brown) (sample 3185). **C.** White grain is osmium $(Os_{0.63}Ir_{0.34}Ru_{0.03})$. Colloform intergrowth consists of osmium (white material) and Ir–Fe alloy $[(Ir,Os,Ru)_{0.66}(Fe,Ni)_{0.34}]$ (black material) (sample 31–12). **D.** Irregular, colloform grain of osmium $(Os_{0.64}Ir_{0.36})$ (white material) and Ir–Fe alloy $(Ir_{0.66}Fe_{0.34})$ (black material) (sample 21–10). **E.** Irregular grain of awaruite $[Ni_{0.74}Fe_{0.24}(Cu,Co)_{0.02}]$ with fritted margin (sample 26–9). **F.** Intergrowth of native iron (round, white grain) and Fe–Mn alloy brownish white grain; contact emphasized) (sample 38–10). Matrix in all cases: epoxy.

TABLE 2. REPRESENTATIVE COMPOSITIONS OF Pt–Fe AND Pt–Os–Fe ALLOYS FROM THE LUOBUSA CHROMITITES

Sample	17-9	21-1	19-2	23-123	23-129	42-23	22-1A	23-53
Os wt.%	0.00	0.00	0.00	0.00	0.00	0.00	10.55	0.00
Pt	89.80	86.50	85.33	82.90	81.36	77.70	76.88	84.64
Rh	0.00	3.99	2.62	4.24	4.44	2.23	6.67	3.85
Fe	10.20	9.51	9.80	9.64	11.40	9.81	5.89	10.29
Ni	0.00	0.00	2.24	1.50	2.80	1.24	0.00	1.23
Co	0.00	0.00	0.00	1.73	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	9.03	0.00	0.00
Total	100.00	100.00	99.99	100.01	100.00	100.01	99.99	100.01
Os at.%	0.00	0.00	0.00	0.00	0.00	0.00	8.95	0.00
Pt	71.59	67.96	64.66	61.26	58.57	52.49	63.58	64.13
Rh	0.00	5.94	3.76	5.94	6.06	2.86	10.46	5.53
Fe	28.41	26.10	25.94	24.88	28.67	23.15	17.02	27.24
Ni	0.00	0.00	5.64	3.68	6.70	2.78	0.00	3.10
Co	0.00	0.00	0.00	4.23	0.00	0.00	0.00	0.00
Cu	0.00	0.00	0.00	0.00	0.00	18.73	0.00	0.00

Approximate formulas: 17-9: $Pt_{0.72}Fe_{0.28}$, 21-1: $(Pt,Rh)_{0.74}Fe_{0.26}$; 19-2: $(Pt,Rh)_{0.69}(Fe,Ni)_{0.31}$; 23-123: $(Pt,Rh)_{0.67}(Fe,Ni,Co)_{0.33}$; 23-129: $(Pt,Rh)_{0.64}(Fe,Ni)_{0.36}$; 42-23: $(Pt,Rh)_{0.55}(Fe,Cu,Ni)_{0.45}$; 22-1A: $(Pt,Rh,Os)_{0.83}Fe_{0.17}$; 23-53: $(Pt,Rh)_{0.70}(Fe,Ni)_{0.30}$.

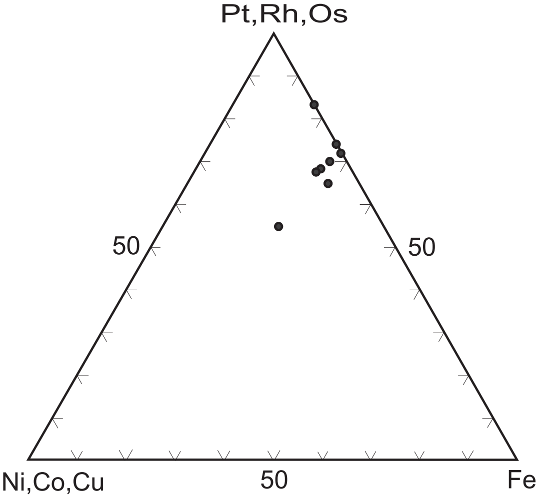

FIG. 5. Triangular diagram showing compositional variation of grains of Fe–Ni–Pt alloy (atomic proportions) in the Luobusa chromitites in terms of Pt, Rh, Os – Ni, Co, Cu – Fe.

Os–Ir–Ru alloy (Figs. 4C, D). Single grains are commonly associated with grains of Ni–Fe alloy (Fig. 4B) or native Ni (> 90 at.% Ni), whereas the colloform varieties are associated with osmium (Fig. 4C).

Concentrations of Ir and Ni vary widely, whereas the Fe contents are relatively constant (mostly between 15 and 25 at.%) (Table 3). Some of these grains also contain small amounts of Ru, Os and Cu. Except for one grain that contains 94.7 wt% Ir, the (Ir + Os + Ru)/(Fe + Ni + Cu) value ranges from 0.2 to 2.1.

Ir–Ni–Fe alloys with PGE:BM proportions ranging from 1.5 to 5 have been reported in chromitites of the Kempirsai ophiolite (Melcher *et al.* 1997).

Base-metal alloy

Grains of base-metal alloy range widely in composition but generally fall into one of three groups: high-Fe, high-Ni, and Fe–Co alloys. The most common variety in the Luobusa chromitites is awaruite (Ni_3Fe), which typically occurs as anhedral grains about 0.2–0.5 mm in diameter, with a pitted or corroded appearance (Fig. 4E). Most of these grains have a composition very close to the ideal formula, although some contain small amounts of Cr and Cu. Two grains have relatively high Ni contents, 84.5 and 92.5 at.% Ni (samples 26–2 and 2–7, respectively, in Table 4), higher than the approximate stoichiometric values, 72–74 at.% Ni.

The other grains of Fe–Ni alloy have Fe:Ni values ranging from 0.65 to 8.63 (Fig. 6). All but one of these grains also contain varying amounts of Cr, from 1.02 to 20.29 at.% (Table 4). A few grains also contain small amounts of Mn and Cu. Two grains are Fe–Co alloy with a ratio Fe/Co essentially equal to 1 (Table 4, Fig. 6).

Awaruite has been reported from a number of localities in association with Ni sulfides in serpentinized ultramafic rocks (*e.g.*, Chamberlain *et al.* 1965, Dick 1974, Melcher *et al.* 1997) and is usually considered to be a secondary mineral.

Native Fe, native Si and Fe silicides

Native Fe occurs in two forms in the Luobusa chromitites, as small, round globules intergrown with an Fe–Mn alloy (Fig. 4F) and as anhedral masses of acicular crystals (Fig. 7A). The composition of these grains is close to 100% Fe, although some have minute amounts of Mn and Si (Table 5). Four grains of pure Si have also been found in the Luobusa chromitites (Table 5); they occur either as an intergrowth with an Fe silicide (Fig. 7B) or as inclusions in SiC. To our knowledge, native Si has not previously been reported from chromitites and is known only as inclusions in diamonds from kimberlites, although Bird & Weathers (1975) reported elemental silicon as inclusions in little altered "josephinite" (awaruite) from southwestern Oregon.

Anthropogenic contamination is always a possibility, but we believe this is not the case for the Luobusa samples. No such grains were found in the granite control sample, which was processed in exactly the same way as the chromite samples. In addition, the variety of native metals (C, Si, Fe, Au, Cu, Ni, Cr) is high, and some of them are intergrown with alloys, such as Fe–Si and Fe–Mn. Finally, some of the native Si occurs as inclusions in Fe–Si alloy (Fig. 7B) and in euhedral SiC crystals, an association difficult to explain by contamination. A somewhat similar assemblage of native

TABLE 3. REPRESENTATIVE COMPOSITIONS OF Ir–Ni–Fe ALLOY FROM THE LUOBUSA CHROMITITES

Sample	31-15	31-17	31-12	31-10	31-7	35-5	35-4	35-3	24-17	31-6	24-11	9-2	24-14
Os wt.%	0.00	0.00	3.50	0.00	3.78	1.36	3.05	12.78	0.00	0.00	0.00	0.00	0.00
Ir	94.73	86.40	83.16	85.87	83.01	81.40	78.23	65.82	64.67	58.08	55.24	40.49	39.34
Ru	1.13	1.16	0.26	1.62	1.07	0.89	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.73	9.51	11.08	9.77	9.52	14.38	8.79	6.85	10.98	11.29	9.82	11.49	11.03
Ni	3.42	2.93	1.99	2.75	2.61	1.96	9.92	14.55	23.95	29.69	34.94	47.08	48.64
Cu									0.39	0.93		0.94	0.98
Total	100.01	100.00	99.99	100.01	99.99	99.99	99.99	100.00	99.99	99.99	100.00	100.00	99.99
Os at.%	0.00	0.00	2.68	0.00	2.93	0.98	2.14	8.61	0.00	0.00	0.00	0.00	0.00
Ir	85.66	65.99	63.07	65.33	63.77	57.99	54.31	43.89	35.52	29.49	27.15	17.08	16.42
Ru	1.94	1.68	0.38	2.30	1.56	1.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	2.27	25.00	28.93	25.49	25.17	35.26	21.00	15.72	20.76	19.73	16.61	16.68	15.85
Ni	10.13	7.33	4.94	6.85	6.57	4.57	22.55	31.77	43.08	49.36	56.24	65.04	66.49
Cu	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.65	1.43	0.00	1.20	1.24

Approximate formulas: 31-15: $(Ir,Ru)_{0.88}(Ni,Fe)_{0.12}$; 31-17: $(Ir,Ru)_{0.68}(Fe,Ni)_{0.32}$; 31-12: $(Ir,Os,Ru)_{0.66}(Fe,Ni)_{0.34}$; 31-10: $(Ir,Ru)_{0.68}(Fe,Ni)_{0.32}$; 31-7: $(Ir,Os,Ru)_{0.68}(Fe,Ni)_{0.32}$; 35-5: $(Ir,Ru,Os)_{0.60}(Fe,Ni)_{0.40}$; 35-4: $(Ir,Os)_{0.56}(Ni,Fe)_{0.44}$; 35-3: $(Ir,Os)_{0.53}(Ni,Fe)_{0.47}$; 24-17: $(Ni,Fe)_{0.64}Ir_{0.36}$; 31-6: $(Ni,Fe)_{0.70}Ir_{0.30}$; 24-11: $(Ni,Fe)_{0.73}Ir_{0.27}$; 9-2: $(Ni,Fe)_{0.83}Ir_{0.17}$; 24-14: $(Ni,Fe)_{0.83}Ir_{0.17}$.

metals and carbides has also been reported in alpine ultramafic rocks in the Koryak Highland (Rudashevsky *et al.* 1987).

The Fe silicide from Luobusa forms subrounded grains 0.1–0.5 mm in size, some of which have fritted margins (Fig. 7B). Most of the grains have relatively uniform compositions with 69.6–71.1 at.% Si and 28.9–30.4 at.% Fe (Table 5), resulting in an Fe:Si ratio of approximately 3:7. One grain is close to pure Si in composition with only 0.1 at.% Fe (Table 5). Several grains of Fe silicide are intergrown with native Si (Fig. 7B).

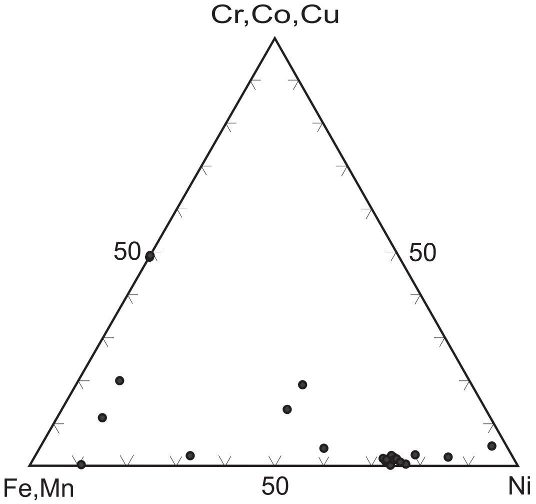

FIG. 6. Triangular diagram showing compositional variations in BM alloys in the Luobusa chromitites in terms of Cr, Co, Cu – Fe, Mn – Ni.

Other minerals

Associated with the alloys is a wide variety of other minerals, the most interesting of which include diamond, moissanite (SiC), an unnamed chromium carbide and graphite (Hu 1999). The crystals of diamond are mostly euhedral octahedra and dodecahedra between 0.2 and 0.7 mm in diameter, although a few twinned and broken grains also are present. The largest grain is 0.83 mm across and contains several Fe–Mg silicate inclusions. Moissanite occurs as small, euhedral crystals up to about 0.5 mm across or as smaller fragments of broken crystals. It ranges widely in color from deep blue, to green to colorless. The unnamed chromium carbide forms steel-grey, acicular crystals up to 0.5 mm long. Graphite is abundant and forms tabular prisms, 0.1–0.7 mm long, with clear hexagonal symmetry (Hu 1999).

DISCUSSION

Natural alloys associated with ophiolites and ultramafic rocks have been commonly interpreted either as secondary minerals formed by alteration or primary magmatic inclusions. Secondary alloys typically occur in cracks in chromite or in serpentine veins (Dick 1974, Stockman & Hlava 1984, Melcher *et al.* 1997). They are mainly Ru-rich Os–Ir alloys (commonly containing small amounts of BM elements) and BM alloys. These PGE alloys usually have a porous appearance, and are typically associated with PGE sulfides (*e.g.*, laurite–erlichmanite).

Those alloys interpreted as being primary typically occur as inclusions in chromian spinel, either as individual grains or composite phases with PGE–BM sulfides. The most commonly reported primary alloy is Os–Ir with less than 10 at.% Ru, which may or may not

TABLE 4. COMPOSITIONS OF REPRESENTATIVE BASE-METAL ALLOYS FROM THE LUOBUSA CHROMITITES

Sample	23-15	30-3-1	30-25	30-18	26-9	26-4	2-18B	26-2	2-18	2-7	16-15	23-104	2-12	2-3	16-30
Fe wt.%	25.22	24.95	24.74	24.34	23.26	18.65	36.92	12.41	39.77	2.42	88.19	72.08	64.27	33.71	49.38
Ni	74.78	72.58	72.88	73.82	74.61	79.05	59.32	84.86	48.38	92.18	11.81	8.84	32.69	48.41	0.00
Cr	0.00	0.00	0.00	0.00	0.00	2.15	3.70	0.00	11.28	0.00	0.00	19.08	0.93	17.88	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.16	0.06	0.00	0.17	0.00	0.00	0.00	1.02	0.00	0.00
Cu	0.00	0.00	0.71	0.68	1.17	0.00	0.00	2.70	0.40	5.39	0.00	0.00	1.10	0.00	0.00
Co	0.00	2.47	1.66	1.16	0.97	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	50.61
Total	100.00	100.00	99.99	100.00	100.01	100.01	100.00	99.99	100.00	99.99	100.00	100.00	100.01	100.00	99.99
Fe at.%	26.17	25.90	25.70	25.28	24.19	19.36	37.91	12.99	40.40	2.55	88.70	71.38	65.33	34.06	50.73
Ni	73.83	71.67	72.02	72.95	73.78	78.07	57.95	84.51	46.76	92.45	11.30	8.33	31.62	46.54	0.00
Cr	0.00	0.00	0.00	0.00	0.00	2.40	4.08	0.00	12.31	0.00	0.00	20.29	1.02	19.40	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.17	0.06	0.00	0.18	0.00	0.00	0.00	1.05	0.00	0.00
Cu	0.00	0.00	0.65	0.62	1.03	0.00	0.00	2.48	0.36	4.99	0.00	0.00	0.98	0.00	0.00
Co	0.00	2.43	1.63	1.14	0.96	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00	49.27

Approximate formulas: 23-15: $Ni_{0.74}Fe_{0.26}$; 30-3-1: $Ni_{0.72}Fe_{0.26}Co_{0.02}$; 30-25: $Ni_{0.72}Fe_{0.26}(Co,Cu)_{0.02}$; 30-18: $Ni_{0.73}Fe_{.25}(Co,Cu)_{0.02}$; 26-9: $Ni_{0.74}Fe_{0.24}(Cu,Co)_{0.02}$; 26-4: $Ni_{0.78}Fe_{0.20}Cr_{0.02}$; 2-18B: $Ni_{0.58}Fe_{0.38}Cr_{0.04}$; 26-2: $Ni_{0.85}Fe_{0.13}Cu_{0.02}$; 2-18: $Ni_{0.47}Fe_{0.41}Cr_{0.12}$; 2-7: $Ni_{0.92}Fe_{0.03}Cu_{0.05}$; 16-15: $Fe_{0.89}Ni_{0.11}$; 23-104: $Fe_{0.72}Cr_{0.20}Ni_{0.08}$; 2-12: $Fe_{0.66}Ni_{0.32}(Cr,Cu)_{0.02}$; 2-3: $Ni_{0.47}Fe_{0.34}Cr_{0.19}$; 16-30: $Fe_{0.51}Co_{0.49}$.

be associated with PGE sulfides. Pt–Fe and Ir–Fe–Ni alloys are also typically interpreted as primary phases.

Secondary alloys in the Luobusa chromitites

The Fe- and Ni-bearing Os–Ir–Ru alloys in Luobusa are similar in composition to the porous, Ru-rich alloys and the laurite–erlichmanite grains in Kempirsai (Melcher *et al.* 1997), southwestern Oregon (Stockman & Hlava 1984), and Samar, Philippines (Nakagawa & Franco 1997). We interpret them to be alteration products of PGE sulfides. There is convincing evidence that primary PGE–BM sulfide phases may become unstable during postmagmatic, supergene evolution of the ultramafic hosts (Stockman & Hlava 1984, Bowles 1986), and that the PGE phases can be modified by the mobilization of platinum-group elements at relatively low temperatures. For example, the porous grains of Ru-rich alloy in chromitites of southwestern Oregon are believed to have formed by desulfurization of primary laurite during serpentinization (Stockman & Hlava 1984).

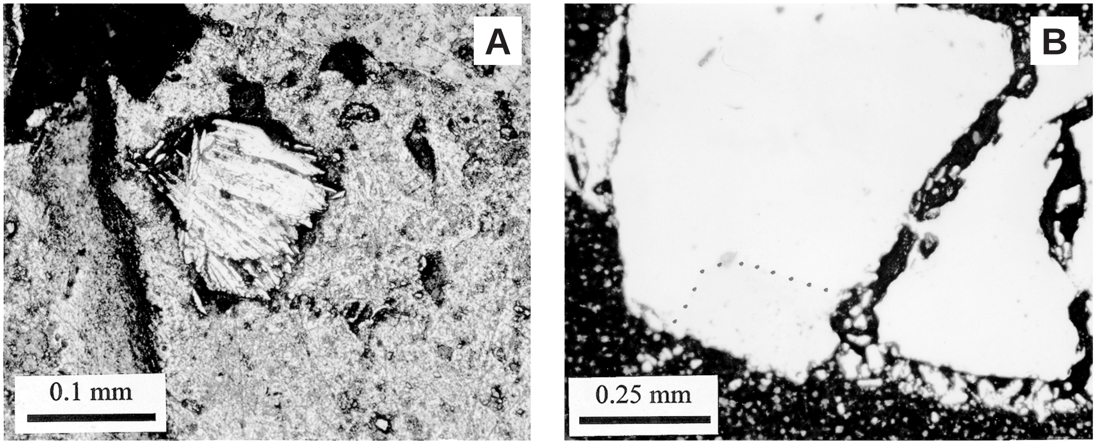

FIG. 7. Reflected-light photomicrographs of native iron and Fe silicide grains in the Luobusa chromitites. A. Irregular grain of native iron with an acicular habit (sample 23–17). B. Ovoid grain of Fe silicide ($Si_{0.69}Fe_{0.31}$) with fritted margins. This grain contains a small patch of native Si below the dotted contact (sample 38–2). Matrix in both cases: epoxy.

TABLE 5. REPRESENTATIVE COMPOSITIONS OF Fe SILICIDES AND NATIVE Si AND Fe IN THE LUOBUSA CHROMITITES

Sample	12-22	23-3	8-1	23-6	38-2	30-28b	4-2	2-2	23-17	16-16	38-3a	35-31	4-6	31-2
Si wt.%	55.26	55.08	53.78	53.51	53.36	99.89	100.00	100.01	0.17	0.65	100.00	100.00	100.00	100.00
Fe	44.74	44.92	46.22	46.48	46.64	0.11	0.00	0.00	98.91	97.53	0.00	0.00	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.91	1.82	0.00	0.00	0.00	0.00
Total	100.00	100.00	100.00	99.99	100.00	100.00	100.00	100.01	99.99	100.00	100.00	100.00	100.00	100.00
Si at.%	71.07	70.92	69.82	69.60	69.47	99.94	100.00	100.00	0.38	0.66	100.00	100.00	100.00	100.00
Fe	28.93	29.08	30.18	30.40	30.53	0.06	0.00	0.00	98.70	97.72	0.00	0.00	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.92	1.43	0.00	0.00	0.00	0.00

Approximate formulas: 12-22: $Si_{0.71}Fe_{0.29}$; 23-3: $Si_{0.71}Fe_{0.29}$; 8-1: $Si_{0.70}Fe_{0.30}$; 23-6 $Si_{0.70}Fe_{0.30}$; 38-2: $Si_{0.69}Fe_{0.31}$; 30-28b: $Si_{0.999}Fe_{0.001}$; 4-2: $Si_{1.00}$; 2-2: $Si_{1.00}$; 23-17: $(Fe,Mn)_{0.996}Si_{0.004}$; 16-16: $(Fe,Mn)_{0.984}Si_{0.006}$; 38-3a: $Si_{1.00}$; 35-31: $Si_{1.00}$; 4-6: $Si_{1.00}$; 31-2: $Si_{1.00}$.

The formation of native PGEs and alloys as a result of low-temperature alteration has also been reported from numerous PGE-bearing chromitites (Prichard & Tarkian 1988, McElduff & Stumpfl 1990, Nilsson 1990, Garuti & Zaccarini 1997). The alteration of laurite to form native Ru at a low temperature was conclusively demonstrated in chromian spinel of the Ronda massif in Spain (Torres-Ruiz *et al.* 1996, Garuti & Zaccarini 1997).

The porous texture seen in grains of Ru-rich Os–Ir alloy elsewhere has been explained by exposure of PGE sulfide inclusions along cracks in chromian spinel, which under conditions of low sulfur activity, would lead to mobilization of PGEs in the order of Ru < Os < Rh < Ir < Pd < Pt (Bowles 1986, Stockman & Hlava 1984). During the desulfurization process, some BM elements may enter the alloys to form compositions similar to those encountered at Luobusa. Inclusions farther from cracks would be protected by the host grains of chromian spinel and be little affected. This process may be responsible for the formation of the Fe–Ni–Cr alloys at Luobusa.

Thus, on the basis of their similarity to secondary phases elsewhere, the Fe- and Ni-bearing and Ru-rich Os–Ir–Ru alloys in the Luobusa chromitites are interpreted as products of low-temperature alteration of primary PGE phases.

It seems likely that the BM alloys, and at least some of the native elements found the Luobusa chromitites, also are secondary in origin. Ni–Fe alloy (awaruite) has been demonstrated to be a secondary mineral in the Josephine ophiolite, produced during serpentinization of peridotite (Dick 1974), and we infer such a mode of origin for this mineral at Luobusa. Some of the native Fe in Luobusa occurs as round globules (Fig. 4F) suggesting formation as melt droplets. However, these could also represent globules of immiscible sulfide that were later modified by alteration.

The origin of the Fe silicide and native Si is not clear. These phases have not been reported in secondary assemblages, and the fritted margins of some of the grains of Fe silicides suggest reaction with a melt. We tentatively include them with the primary alloys discussed below.

Primary alloys in the Luobusa chromitites

Pt–Fe, Os–Ir, and Ir–Ni–Fe alloys are typically interpreted as primary phases because they are incorporated in crystals of chromian spinel (Stockman & Hlava 1984, Augé 1988, Melcher *et al.* 1997) and are commonly believed to be products of early crystallization of the melts from which the chromitites formed. Roeder & Jamieson (1992) showed experimentally that Pt–Fe alloy co-crystallizing with primary chromian spinel at 1200°C and $f(O_2)$ equivalent to FMQ buffer [log $f(O_2)$ = –8.41] should have a Fe/(Fe + Pt) between 0.20 and 0.25. They further showed that the alloy compositions are relatively insensitive to changes in composition of the chromian spinel. These values accord well with those of Grove (1981), who indicated that Pt–Fe alloys should contain 78.4 at.% Pt if they formed in equilibrium with natural basalts at the QFM buffer over a wide range of temperature.

Most of the Pt–Fe alloy grains at Luobusa have significantly lower Pt contents (52.5 to 71.6 at.%) and slightly higher Fe/(Fe + Pt) ratios (0.20–0.32) than the experimentally determined values. If the Fe/(Fe + Pt) values encountered at Luobusa reflect primary values, they suggest crystallization under more reducing conditions than those assumed in the experiments of Roeder & Jamieson (1992). It is very difficult to estimate the $f(O_2)$ conditions under which the magnesiochromite formed at Luobusa. The magnesiochromite compositions suggest crystallization under oxidizing conditions, whereas the presence of many reduced phases (*e.g.*, graphite, diamond, Cr, SiC, a chromium carbide, Si) suggests low fugacities of oxygen. Either these reduced phases formed later than the magnesiochromite or some special conditions allowed them to be preserved in an oxidizing environment.

We suggest that the Pt–Fe, Os–Ir and Ir–Fe–Ni alloys and the Fe silicide are out of equilibrium with the host magnesiochromite, and that the alloys and the magnesiochromite did not crystallize from the same melts. This interpretation is based on the following arguments:

1. Experimental studies have shown that an Os–Ir–Ru alloy is an extremely refractory phase, with temperatures of formation much higher than those inferred for the crystallization of magmatic chromitites at Luobusa or even for formation of silicate melts in the upper mantle. In particular, Os–Ir alloys melt in the range of 2443°C to 3050°C (Bird & Bassett 1980). Even though these temperatures would be significantly reduced in silicate melts, they may still be higher than the melting temperature of hydrous mantle material presumed to be the source of the boninitic melts from which the magnesiochromite crystallized.

2. Peach & Mathez (1996) have demonstrated experimentally that Os–Ir alloys are not stable in silicate melts in nature. To crystallize magmatic Os–Ir alloys, mantle-derived melts should have Ir contents in the range of thousands of ppb. However, Ir concentrations in natural melts range from <0.02 ppb in MORB (Hertogen *et al.* 1980) to <0.23 ppb for boninites (Hamlyn *et al.* 1985). Thus, Peach & Mathez (1996) concluded that ".. Os–Ir alloys observed as inclusions in chromite cannot represent early crystallized phases."

3. The alloys in the Luobusa chromitites are associated with a variety of exotic minerals, such as diamond, SiC, an unnamed chromium carbide, Fe silicide and native Si. Iron silicide is known only as an inclusion in diamonds, suggesting an ultra-high-pressure origin. SiC has also been found as inclusions in diamond and is generally considered an ultra-high pressure mineral in nature. We believe that these minerals are xenocrysts derived from deep mantle sources (Hu 1999).

4. Most of the osmium alloys in Luobusa plot in the 1-bar pressure miscibility gap determined experimentally by Bird & Bassett (1980) (Fig. 3), although they lie outside the field defined by natural specimens (Harris & Cabri 1991). Bird & Bassett (1980) suggested that at high pressures, the miscibility gap in the binary system Os–Ir is shifted toward the Ir end. The Luobusa alloys plot outside this presumed high-pressure gap, suggesting formation at relatively high pressures.

Some of the alloys may have formed by alteration of pre-existing minerals or by exsolution, as suggested by Peach & Mathez (1996). However, formation by either of these processes seems unlikely given the nature, morphology and distribution of the grains. Typically, these alloys are relatively pure Os–Ir, Pt–Fe, and Ir–Fe–Ni, occurring in zoned crystals (*e.g.*, Figs. 2C, D, F). The boundaries between zones are sharp and well defined, not what would be expected if the grains formed by alteration. Some of the grains occur as inclusions, completely enclosed in magnesiochromite and are not associated with PGE-bearing sulfides or other possible parental minerals (Fig. 2A). Those alloys lying between grains (*e.g.*, Fig. 2B) are Ru-rich varieties, assumed to be secondary in origin. Finally, some of the grains have a rounded or ovoid shape with a smoothly curving boundary (Figs. 2C, D), which suggests formation by crystallization from melt globules.

Because the "primary" alloys at Luobusa do not seem to have crystallized from the boninitic melts that formed the chromitites or to have formed by alteration or exsolution, and because they are associated with a variety of UHP minerals, we infer that they are xenocrysts derived from a deep mantle source. In this model, they could represent phases left in the mantle during early stages of differentiation of Earth. They would have been transported to relatively shallow depths by a rising mantle plume, and then incorporated into the melts from which the chromitites eventually crystallized.

Natural alloys tend to be inert in many geological environments (Feather 1976), but can be modified under certain conditions (Bowles 1986). Experimental evidence suggests that PGE alloys react relatively rapidly with silicate melt (Roeder & Jamieson 1992). Thus, it is not clear how the PGE grains at Luobusa remained essentially unchanged in chemical composition and morphology after being incorporated into a boninitic melt, but other ultra-high pressure minerals, such as diamond and moissanite, show the same lack of reaction. Diamond has recently been reported from volcaniclastic komatiite (Capdevila *et al.* 1999), which formed from melts similar in composition to the boninitic magmas parental to the Luobusa chromitites. Although these crystals of diamond have "low-relief surface features" suggestive of transport in a strongly reactive magma, they maintain a cubo-octohedral morphology. They are interpreted as xenocrysts from depths greater than 150 km (Capdevila *et al.* 1999).

Tredoux *et al.* (1995) suggested another possible explanation for the origin of 'primary' PGE alloys. They proposed that the PGE occur in melts as metallic clusters rather than as individual atoms, and that these clusters are stabilized by surface absorption of ligands, such as S, As, Sb and Te. Such clusters would significantly change the way in which PGE behave in a magma and tend to overcome the problem of crystallization of alloys from melts with very low PGE contents. They suggested that such clusters could coalesce in silicate melts to form PGE alloys, which then would act as centers of nucleation for early-forming silicates and oxides. Such PGE clusters are readily formed experimentally (Schmid 1985), but there is no direct evidence for their existence in natural systems. Lacking such evidence and given the association of PGE alloys in Luobusa with UHP phases such as diamond and moissanite, we favor the xenocrystic model described above.

CONCLUSIONS

A variety of PGE and BM alloys occur in the chromitites of the Luobusa ophiolite where they are associated with exotic minerals such as diamond, graphite, SiC, an unnamed chromium carbide, and native Si. The BM alloys and Ru-rich PGE alloys are similar to secondary phases found elsewhere. We interpret them to be the products of alteration of PGE and BM sulfides.

On the basis of their textural relationships, chemical compositions and mineralogy, we suggest that the Pt–Fe, Os–Ir, and Ir–Ni–Fe alloys, along with Si–Fe and possibly native Si, are xenocrysts derived from a mantle source below 150 km. We suggest that after formation in the mantle, these minerals were transported to shallower depths by a rising plume, where they were captured by the boninitic melts from which the chromitites crystallized. It is not clear how they survived transport in a such a hot silicate melt. One possibility is that they were transported originally in large xenoliths that disaggregated at a relatively late stage as the melt was undergoing rapid cooling.

After crystallization of the Luobusa chromitites, possibly during emplacement of the ophiolite, some of the PGE-bearing sulfides were exposed along fractures in the magnesiochromite and were altered to form BM alloys and BM-bearing Os–Ir–Ru alloys.

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