Os-Ir-Ru Alloys from the Kunar Ultramafic Complex, Northeastern Taimyr, Russia: Evidence for Residual Origin Inferred from Mineral Chemistry and Osmium Isotopes

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Introduction

Serpentinized harzburgites within the Chelyuskin and Stanovoi ophiolite belts, northern Taimyr Peninsula, were recognised by Bezzubtsev et al. (1986). It has been proposed that Taimyr ophiolites and island-arc magmatic complexes were formed and subsequently emplaced onto the Arctic Siberian Craton passive margin around 750 Ma and 600 Ma, respectively (Vernikovsky and Vernikovskaya, 2001). However, the age of ultramafic protoliths are poorly constrained. To address this problem, a combined mineralogical and osmium-isotope study of detrital platinum-group minerals (PGM) from the Kunar Ultramafic Complex, which forms part of the Chelyuskin ophiolite, was undertaken. The aims of this study are to ascertain the origin of PGM, determine the isotopic source of platinum-group elements (PGE) and to provide age constraints on the formation of ultramafic protolith(s).

Geology and Sample Location

Ultramafic rocks of the Kunar Complex (Fig. 1) are composed mainly of metaperidotites (serpentinized harzburgites and dunites). Metaperidotites trend northeast and frequently boardered by gabbroic rocks, narrow zones of serpentinite melange, greenschists and listwaenites. Other rocks in the Chelyuskin ophiolite are tholeiitic basalts, dolerites of a dyke-sill complex and sheeted plagiogranites (Vernikovsky, 1996). U-Pb and Sm-Nd isotopic studies show that the plagiogranites of the Chelyuskin ophiolite formed between 850 and 740 Ma. More detailed information on the geology of the Chelyuskin ophiolite belt has recently been summarized by Vernikovsky and Vernikovskaya (2001).
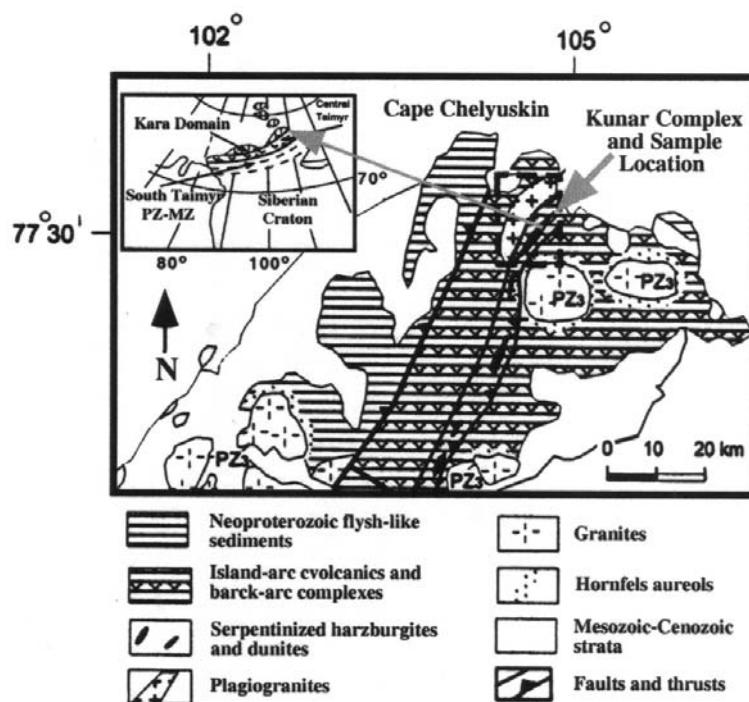

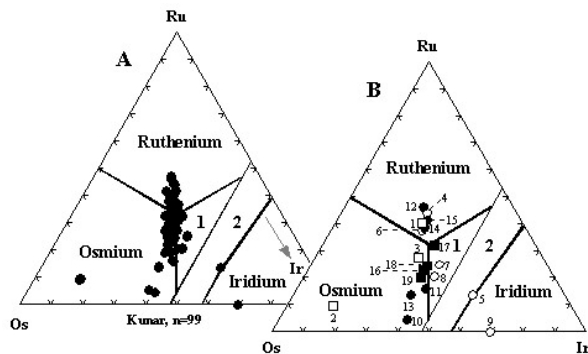**Figure 1.** Schematic geological map of northeastern Taimyr.

Figure 2. Composition of Os-Ir-Ru in the ternary diagram Ru-Os-Ir, at.%. Fig. 2B, PGM grains measured by NTI-MS, subdivided according to their Os-isotope composition: open squares refer to PGM with $^{187}Os/^{188}Os$ less than 0.1202, open circles - $^{187}Os/^{188}Os$=0.1214-0.1225, filled circles - $^{187}Os/^{188}Os$=0.1229-1231, filled squares - $^{187}Os/^{188}Os$=0.1237-0.1241. Numbers 1-19 correspond to the same numbers in Table 1.

This study is based on 33 Os-rich PGM grains (size range between 0.25 and 0.5 mm), which were sampled from a gold production concentrate in the area of the Unga River. The PGM studied have been derived from the Unga Jurassic placer deposit (Gavrish, 2000), which is closely associated with the Kunar ultramafic Complex (Fig. 1).

Analytical Methods

Initially, morphology of PGM grains, represented by individual crystals and polymineral aggregates, was documented by scanning electron microscopy (SEM). The grains were, then, mounted and polished, described and analyzed by electron microprobe analysis (EMPA) (Camscan-4 with energy-dispersive spectrometer Link-10 000 and wavelength spectrometer Microspec, JSC Mekhanobr-Analyt, St.-Petersburg, Russia and ARL-SEMQ microprobe with four wavelength-dispersive spectrometers and equipped with a LINK energy dispersive analyser, Institute of Geological Sciences, University of Leoben, Austria). Finally, 19 PGM grains were removed from the resin and the osmium isotope ratios determined in the individual PGM by negative thermal ionization mass-spectrometry (NTI-MS). Precision of the osmium isotope determinations was found to be 0.3 relative per cent. Osmium isotopes were determined by one-tape detection of negative OsO_3^- ions formed on the cathode surface at temperatures of 700-1400°C (Kostoyanov and

Pushkarev, 1998). The method allows the analysis of individual PGM weighing as little as 10^{-7}g and containing more than 10 wt. % of osmium. The amount of single PGM grains was sufficient to maintain the signal from one of the most abundant Os isotopes (^{190}Os) at 10^{-13} - 10^{-14} Å. Measured isotope ratios were normalized by taking into account both isobar and mass-fractionation effects. The mass-fractionation effect was considered to be exponentially related to the detected ion mass. Further details on the method and analytical precisions are given in Malitch et al. (2000).

Results and Discussion

PGE mineralogy. A diversity of alloys of Os-Ir-Ru system (IPGE alloys) have been observed. According to the classification of Harris and Cabri (1991) they comprise osmium, ruthenium, rutheniridosmine and iridium. Most of the PGM grains are monophase (28 cases). Five polyminerallic grains (e.g., 1-2, 3-4, 3-5, 5-2 and 6-1) are dominated by IPGE alloy, with minor amounts of one or several other PGM (e.g., Pt-Fe alloy close to Pt_3Fe, chengdeite Ir_3Fe, cuproiridsite $CuIr_2S_4$, laurite RuS_2, unnamed Os-Ir sulfide $(Os,Ir)S_2$, irarsite IrAsS and moncheite $PtTe_2$). PGM grains are dominated by osmium alloys [e.g., (Os,Ir,Ru), 17 cases, (Os,Ir), 3 cases and (Os,Ru, Ir), 2 cases], followed by ruthenium [(Ru,Os,Ir), 4 cases], rutheniridosmine [(Ir,Os,Ru), 3 cases], and iridium [(Ir,Os), (Ir,Os,Ru,Pt) and (Ir), one case each] (Fig. 2A). Such diversity of IPGE alloys is not unusual in ophiolite-type complexes (Cabri et al., 1996). The presence of the ruthenium trend in the mineral compositions (Fig. 2A) is, according to Bird and Bassett (1980), due to the formation of these minerals under high mantle pressure conditions.

Os isotope systematics. $^{187}Os/^{188}Os$ ratios and calculated model ages of 19 PGM grains from the Kunar Complex are shown in the Table 1. Since the concentration of Re in all samples is less than 0.05 wt. %, the isotopic effect of ^{187}Re *in situ* radioactive decay can be considered negligible when discussing the analytical data. Hence, the value of $^{187}Os/^{188}Os$ in the PGM under discussion corresponds to that in the source of the ore material at the time of PGM formation. The $^{187}Os/^{188}Os$ ratio and $\gamma Os_{(T=0)}$ in PGM investigated ranges from 0.1094±0.0004 to 0.1241±0.0004 and from -14.10 to -2.56, respectively (Table 1). Calculations using the "Isoplot" program allow the PGM to be divided into several main groups. Excluding 3 PGM grains (1-4, 2-3 and 3-5) with the lowest $^{187}Os/^{188}Os$ values (< 0.1202), at least three PGM groups can

be estimated, with average $^{187}Os/^{188}Os$ values of 0.1217±0.0003 (n=4), 0.1230±0.0004 (n=6) and 0.1239±0.0004 (n=4), respectively (Table 1, expanded uncertainties are within the 95% confidence level). Finally, two remaining values (samples 4-5 and 2-5) are distinctly different from those previously mentioned. These PGM have $^{187}Os/^{188}Os$ values of 0.1021±0.0003 and 0.1025 ±0.0003, respectively. No correlation between chemical composition and isotope content of the samples was discovered (Fig. 2B). Osmium isotope ratios of optically homogeneous PGM crystals are similar to those of polyphase PGM grains.

The identity of the Re/Os ratio for the Earth as the whole and, in particular, for the mantle, which has not changed during its geological history, allows the assumption that model (mantle-derived) Re-Os ages for the mantle derivatives should be close to the real ones in comparison to the similar ratios for the other isotope systems. Model ages may be calculated according to the method proposed by Allegre and Luck (1980) if several assumptions are fulfilled. One of these assumptions is that the Os evolution curve of the mantle is known. A second assumption is that $^{187}Os/^{188}Os$ values in all analyzed PGM samples should not exceed the value of the contemporary undifferentiated mantle material (CHUR). The average initial $^{187}Os/^{188}Os$ ratio for CHUR at 4.56 Ga, commonly used in calculations, ranges from 0.09531 to 0.09600. Accepted average $^{187}Os/^{188}Os$ values for present day mantle vary, 0.12700 (Shirey and Walker, 1998), 0.12736 (Yin et al., 1996) and 0.12960 (Meisel et al., 2001). If model (mantle-derived) ages are calculated assuming chondritic mantle Os evolution curve (T_{ch}, Table 1), contemporary and primary $^{187}Os/^{188}Os$ ratios in undifferentiated mantle reservoir are 0.12736 ±0.00016 and 0.09600 ±0.00035, respectively (Yin et al., 1996). However, if the composition of present day primitive upper mantle (PUM) of Meisel et al. (2001) is considered, the calculated model ages are approximately 0.3 Ga older. The above mentioned PGM groups have average model ages of 0.823±0.045, 0.634±0.060 and 0.503±0.060 Ga, respectively, if chondritic evolution curve is assumed (Table 1). Older model ages for these groups (e.g., 1.123±0.045, 0.938±0.060 and 0.810±0.060 Ga, respectively) are characteristic of PUM estimate. Several groups of Os isotope model ages exemplified by Kunar PGM very likely reflect the polycyclic sequence of partial melting events during the prolonged period of formation of residual ultramafites of the Kunar Complex.

Table 1. *NTI-MS osmium isotope compositions of PGM from the Kunar Complex, Russia.*

N	Sample	Mineral	$^{187}Os/^{188}Os$	$T_{(ch)}$, Ga	$\gamma Os_{(T=0)}$
1	1-4	Ruthenium	0.1094 (4)	2.610	-14.10
2	2-3	Osmium	0.1189 (3)	1.230	-6.64
3	3-5	Osmium	0.1202 (3)	1.040	-5.62
4	2-4	Ruthenium	0.1214 (3)	0.866	-4.68
5	5-3	Iridium	0.1217 (3)	0.823	-4.44
6	6-5	Ruthenium	0.1217 (3)	0.823	-4.44
7	3-3	RIO*	0.1219 (3)	0.793	-4.28
Mean		*Alloys (n=4)*	*0.1217 (3)*	*0.823*	*-4.44*
8	4-5	RIO*	0.1221 (3)	0.765	-4.13
9	2-5	Iridium	0.1225 (3)	0.706	-3.82
10	5-2	Osmium	0.1229 (3)	0.648	-3.50
11	4-3	Osmium	0.1229 (3)	0.648	-3.50
12	4-2	Ruthenium	0.1230 (3)	0.634	-3.42
13	4-1	Osmium	0.1231 (3)	0.619	-3.34
14	64-2	Ruthenium	0.1231 (4)	0.619	-3.34
15	2-1	Ruthenium	0.1231 (4)	0.619	-3.34
Mean		*Alloys (n=6)*	*0.1230 (4)*	*0.634*	*-3.42*
16	3-4	Osmium	0.1237 (3)	0.532	-2.87
17	1-1	RIO*	0.1238 (3)	0.517	-2.80
18	4-4	Osmium	0.1241 (3)	0.474	-2.56
19	6-7	Osmium	0.1241 (4)	0.474	-2.56
Mean		*Alloys (n=4)*	*0.1239 (4)*	*0.503*	*-2.72*

RIO* - rutheniridosmine, $^{187}Os/^{188}Os$ normalized to $^{190}Os/^{188}Os$. (1.98379) (Tuttas, 1992); the parameter $\gamma Os_{(T=0)}$ is the percent deviation of the isotopic composition of a mineral compared with the average Chondritic mantle composition at present.

Most ophiolites in the world are younger than 1 Ga. Their formation ages show distinct peaks in the Late Proterozoic (Late Riphean), Cambro-Ordovician and Jurassic-Cretaceous (Ishiwatari 1994). The question remains open if the final stages of formation of ultramafic source rocks at Kunar are Early Paleozoic or Late Riphean (e.g., 474-532 Ma or 782-839 Ma (n=4) corresponding to $^{187}Os/^{188}Os$ chondritic or PUM evolution curve, respectively). However, Os-isotope sytematics suggests that melt depletion events, recorded by 'unradiogenic' $^{187}Os/^{188}Os$ in PGM from Kunar and several other ophiolite-type complexes worldwide (Fig. 3 in Malitch and Badanina, 2002) are older than the time of their emplacement into crustal levels.

Conclusions

The characteristic feature of PGM from Kunar is the extensive presence of different alloys

of the Os-Ir-Ru system (e.g., osmium, rithenium, rutheniridosmine and iridium). IPGE alloys from Kunar are characterised by 'unradiogenic' $^{187}Os/^{188}Os$ and $\gamma Os_{(T=0)}$ values, indicative of a chondritic or subchondritic mantle source of PGE. These values yield a very wide range of $^{187}Os/^{188}Os$ ratios (0.1094 ± 0.0004 to 0.1241 ± 0.0004) and $\gamma Os_{(t=0)}$ (-14.10 to -2.56), which is almost identical to the Os isotope composition of bedrock Ru-Os sulfides and detrital Os-rich alloys derived from other ophiolite-type ultramafic massifs. This isotopic evidence suggests that locally restricted, but temporally extended, periods of PGM formation took place in the mantle environment. This observation further supports a residual origin of ultramafic rocks from the mantle section of an ophiolite.

Acknowledgements

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