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Are highly siderophile elements (PGE, Re and Au) fractionated in the upper mantle of the earth? New results on peridotites from Zabargad

Gerhard Schmidt [a,*], Herbert Palme [b], Karl-Ludwig Kratz [a], Gero Kurat [c]

[a] Institut für Kernchemie, Johannes Gutenberg-Universität Mainz, Fritz-Straßmann-Weg 2, D-55099 Mainz, Germany
[b] Institut für Mineralogie und Geochemie, Universität zu Köln, Zülpicher Straße 49b, D-50674 Cologne, Germany
[c] Naturhistorisches Museum, Burgring 7, A-1010 Vienna, Austria

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Abstract

Seven peridotite samples from Zabargad Island (Red Sea) were analyzed for highly siderophile elements (HSE), including five platinum-group elements (PGE: Os, Ir, Ru, Rh, Pd) and Re and Au. Petrography and chemical composition of the samples had been published earlier [Kurat, G., Palme, H., Embey-Isztin, A., Touret, J., Ntaflos, T., Spettel, B., Brandstätter, F., Palme, C., Dreibus, G., Prinz, M., 1993. Petrology and geochemistry of peridotites and associated vein rocks of Zabargad Island, Red Sea, Egypt. Mineralogy and Petrology 48, 309–341]. Five samples with chemical compositions typical of upper mantle rocks, from fertile to increasingly depleted mantle (CaO: 3.39 to 0.21%), have Ir concentrations from 1.98 to 3.28 ppb, within the range in spinel and garnet–lherzolites from worldwide occurrences. There is, in Zabargad and in other localities, no systematic dependence of the contents of Ir and other PGE on the degree of fertility of the host rock (amount of cpx) nor on the geologic setting, xenolith or massive peridotite. Two samples, an orthopyroxenite (7.9 ppb Ir) and a plagioclase wehrlite (29.08 ppb) have significantly higher concentrations of all HSE, except Re, reflecting the mobility of these elements in a metasomatized mantle. The more or less unfractionated PGE-patterns and the comparatively low Re contents of the enriched rocks indicate that the PGE were apparently transported with a single mobile phase, presumably sulfides, and that Re is chemically decoupled from the other HSE. However, because of the approximately constant level of PGE in upper mantle rocks, it is unlikely that such phases are the main carriers of PGE in these rocks. Although the CI-normalized patterns of the HSE in the Zabargad samples are to a first order chondritic a detailed inspection reveals deviations from chondritic ratios within about a factor of two, significantly beyond analytical uncertainties. Six of the seven samples show enrichments in Pd (factor of two) and some enrichments in Ru (30%) and Rh (30%) relative to the CI-concentrations of Ir, Os. Rhenium contents are variable and decoupled from the PGE abundances. If the HSEs were added to the Earth's mantle with a late chondritic veneer ratios among these elements should better agree with chondritic ratios. Variations within the groups of chondritic meteorites are too small to explain the observed ‘‘anomalies’’. The fractionated patterns of PGE in the Zabargad rocks either indicate the presence of additional, perhaps local, components of HSEs in the mantle, or they reflect processing of the PGE within the upper mantle, or, alternatively, the

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[*] Corresponding author.

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late veneer hypothesis is invalid. It is important in future work to better define the lateral and/or vertical extent of such anomalies in the Earth's mantle.

Keywords: Highly siderophile elements; Chondritic ratios; Earth's mantle

1. Introduction

Upper mantle material is accessible for investigation as three different rock types: (1) mantle xenoliths associated with kimberlites or alkaline volcanics, (2) alpine peridotites which are assumed to represent slices of the uppermost mantle tectonically emplaced into the crust, and (3) deformed ultramafic rocks at the base of ophiolites (see summary by O'Neill and Palme, 1998). The bulk chemical compositions of these rocks are consistent with the composition of the primitive upper mantle after removal of small and variable fractions of a basaltic component. The most fertile upper mantle rocks closely approach the estimated composition of the primitive upper mantle except for the highly incompatible elements. Typical chemical signatures of upper mantle rocks are (a) high Mg/Fe-ratios, (b) nearly unfractionated (i.e., chondritic) ratios of compatible refractory lithophile elements (Ca, Al, Sc, Yb, etc.), and (c) relatively high contents of siderophile elements, such as Ni, Co, platinum-group elements (PGE), Re and Au (e.g., Jagoutz et al., 1979; Palme and Nickel, 1985). A particularly important signature of mantle rocks is the comparatively high content of PGE, Re and Au. In addition, the CI-normalized patterns of these elements are more or less unfractionated (i.e., relative abundances are chondritic to within a factor of two, often much better), with some depletion of Au, perhaps reflecting low Au in the parent component of the upper mantle. The extremely high metal/silicate partition coefficients of Pd, Ir and Pt recently determined, exclude equilibrium partitioning of PGE, Re and Au between core and mantle, even at very high temperatures and pressures (Borisov et al., 1994; Borisov and Palme, 1995, 1997; Holzheid et al., 1997) supporting the late veneer hypothesis, whereby the last fraction of accreting chondritic material ($< 1\%$) in the formation of the Earth is more or less homogeneously mixed into the mantle after core formation had been completed, i.e., mantle silicates and core metal had not equilibrated after the arrival of the late veneer (Kimura et al., 1974; Chou, 1978; Jagoutz et al., 1979; Morgan et al., 1981; O'Neill, 1991). The late veneer is generally assumed to be representative of chondritic (i.e., unfractionated) meteorites, implying that ratios among the highly siderophile elements (HSEs) in the present mantle are chondritic. Differentiated stony meteorites (e.g., eucrites) would not provide HSEs and iron meteorites appear unlikely for several reasons. They are rare, as seen from the small number of iron meteorite falls. In addition, iron meteorites have, in most cases, strongly fractionated patterns of siderophile elements, unlike the roughly chondritic patterns recorded in upper mantle rocks. Finally, the late veneer has probably delivered S and several non-siderophile elements to the Earth's mantle (see, for example, O'Neill, 1991). Thus, the most plausible candidates for the late veneer component are certainly chondritic meteorites in the broadest sense, which also includes comets. The Earth's mantle should therefore have a basically chondritic signature of HSE. Such a pattern is, however, only defined within about 20% in element ratios. This is the extent of variations in the relative abundances of some of the siderophile elements in different types of chondritic meteorites, such as, for example, the Pd/Ir-ratio.

Approximately chondritic ratios of HSEs in upper mantle rocks were reported by several authors (Morgan et al., 1981; Chou et al., 1983). Recently, Pattou et al. (1996) reported deviations from chondritic Pd/Ir ratios in a series of rocks from spinel lherzolite massifs in the Pyrenean. Non-chondritic Pd/Ir ratios were found earlier by Schmidt (1991) in alpine lherzolitic peridotites from the Eastern Central Alps. Pattou et al. (1996) suggested that the higher than chondritic Pd/Ir ratios may be characteristic of certain mantle reservoirs. This is surprising because the relatively constant level of Ir in upper mantle rocks suggests a well-mixed and relatively uniform component of HSEs in the mantle (Spettel et al., 1991).

It is therefore important to precisely determine the relative abundances of HSEs in mantle rocks of different geological environments and to define possible deviations from chondritic patterns. Such data will provide a test of the late veneer hypothesis, and thus, will lead to a better understanding of the late accretionary history of the Earth.

In this paper, we report new PGE data for spinel lherzolite samples from Zabargad island, an uplifted ultramafic massif in the northern part of the Red Sea (Schmidt et al., 1994).

2. Geological setting and sample description

Peridotitic rocks from the island of Zabargad in the Red Sea have been described by Kurat et al.

Table 1
Major and trace element contents of peridotites and associated vein rocks of Zabargad Island, Red Sea, in wt.% (XRFA) and in μg/g (INAA). Data are from Kurat et al. (1993)

	Z-17 (Amph-harz)	Z-36 (Amp-duni)	Z-13 (Sp-lher)	Z-34 (Sp-pl-lher)	Z-14 (Sp-pl-lher)	Z-31 (Opx-pyro)	Z-26 (Pl-wher)
SiO_2	42.70	41.99	43.74	43.91	43.80	42.64	46.60
TiO_2	0.02	0.06	0.08	0.14	0.09	0.19	0.38
Al_2O_3	0.58	1.53	2.44	3.64	3.06	5.17	5.86
FeO[a]	7.87	8.50	8.46	7.64	8.02	6.12	6.48
MgO	44.17	41.92	40.08	38.24	40.00	31.12	23.46
CaO	0.21	3.39	2.14	3.09	2.01	2.31	13.10
Na_2O	0.04	0.27	0.09	0.32	0.29	0.17	0.32
P_2O_5	< 0.02	0.68	< 0.02	< 0.02	< 0.02	< 0.02	0.02
Total	95.59	98.34	97.03	96.98	97.27	97.12	96.22
100 × Mg	91.43	89.78	89.41	89.92	89.89	86.58	90.06
S	154	215	206	380	439	143	319
Cu[b]	2	1	10	9	8	4	17
Cl	230	970		515	605		840
K	110	545	103	206	140	92	146
Sc	5.26	10.9	13.8	15.3	16.1	18.5	54.1
Cr	2550	2600	2280	2480	2528	3760	1790
Mn	1030	1130	1064	975	950	995	1197
Co	119	97.8	112	108	106	69.4	61.1
Ni	2750	2390	2130	2220	2265	1130	1020
Zn	48	38	50	72	56	53	
Ga		1.26	2.4	3.23	2.8	4.12	6.54
Br	0.17	0.65		0.55	0.35	0.24	1.96
La	0.5	13.8	0.23	0.19	0.21	0.085	0.5
Ce	0.98	34.8	0.59	0.86	0.68	0.3	2.35
Nd	0.47	19.6	0.53	0.64	0.60	0.28	2.5
Sm	0.113	4	0.18	0.252	0.21	0.118	1.06
Eu	0.027	0.774	0.066	0.104	0.083	0.052	0.398
Tb		0.42	0.057	0.075	0.075	0.05	0.27
Dy		2.25	0.38	0.59	0.54	0.39	1.85
Ho		0.44	0.083	0.13	0.13	0.093	0.42
Yb	0.041	0.57	0.25	0.38	0.34	0.33	1.16
Lu	0.006	0.07	0.034	0.059	0.057	0.051	0.173
Hf			0.11	0.15	0.10	0.12	0.46
Ta		0.17	0.007			0.07	
Ir	0.0055	0.0046	0.0056	0.0041	0.0038	0.0053	0.028
Au	0.0006	0.0011	0.0014				0.009
Th	0.23	1.42					
U	0.023	0.17					

[a] Total Fe as FeO. Sulphur analyses G. Dreibus, MPI for Chemistry, Mainz.
[b] Cu data (ICP) from A. Katzemich, University of Köln.

(1982) and Bonatti et al. (1986). Zabargad Island contains three ultramafic bodies which are interpreted to have been tectonically emplaced during the early rifting of the Red Sea in post-Mesozoic time. The ultramafic rocks in these bodies consist of two major groups, the peridotites and the vein rocks within them. The peridotites are divided into three groups: primitive, depleted and metasomatized rocks. The primitive peridotites are represented by pristine spinel lherzolites with chemical compositions approaching the composition of the subcontinental upper mantle (Kurat et al., 1993). Depleted peridotites are mainly harzburgites and some dunites. The most depleted peridotites appear to have the greatest metasomatic additions of incompatible elements (see also Piccardo et al., 1993).

Seven samples from three groups of peridotites from Zabargad were chosen for analysis. Sample locations are given in Kurat et al. (1993). All samples have been previously analyzed by INAA for major and trace element concentrations (see Table 1) and, in addition, a thorough study was made of their petrology and mineralogy (Kurat et al., 1993).

Three samples are described as *primitive peridotites* (Z-13 spinel–lherzolite, Z-14 spinel–plagioclase–lherzolite, Z-34 spinel–plagioclase–lherzolite). The most fertile rocks (Z-14, Z-34) have major and trace element compositions which closely approach the estimated upper mantle composition (e.g., Palme and Nickel, 1985). The CI-normalized rare earth element (REE) patterns are flat at about twice the CI-chondrite level (Fig. 1a). Spinel lherzo-

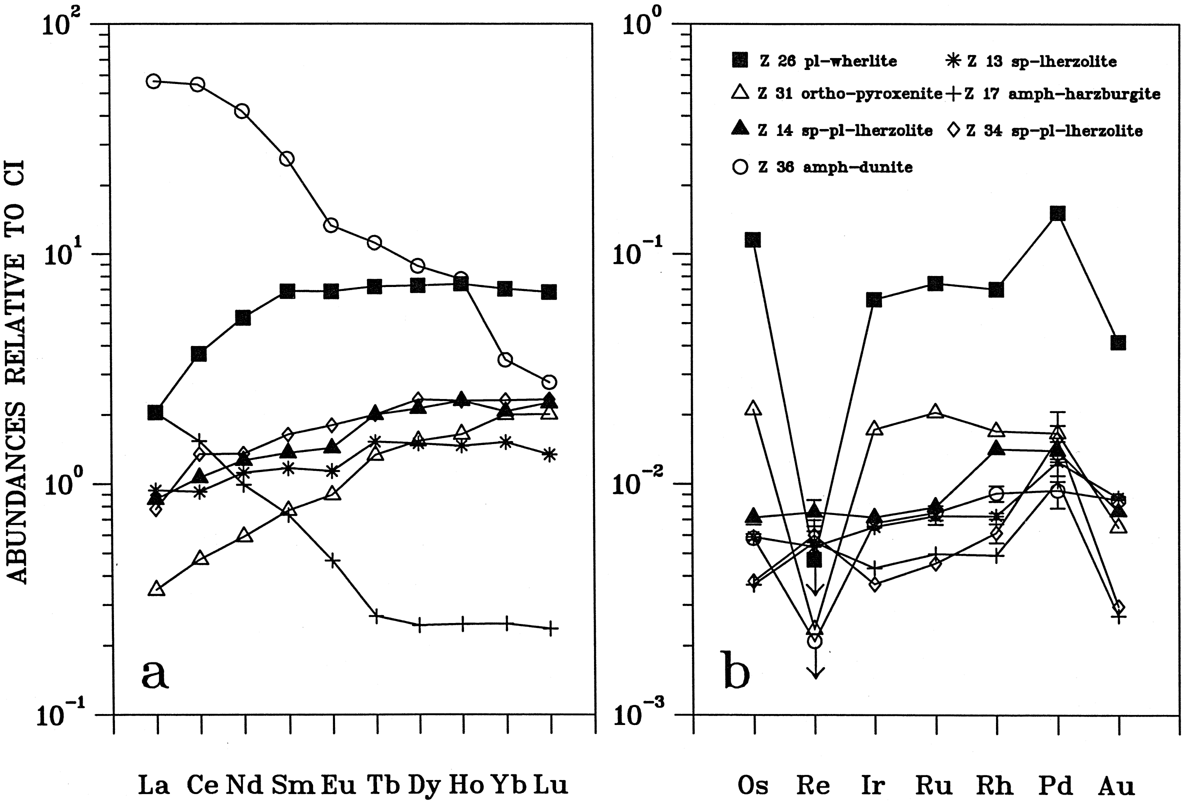

Fig. 1. (a) REE abundances of Zabargad peridotites normalized to CI. The most residual rocks, Z-17 (amphibole–harzburgite) and Z-36 (amphibole–dunite) have large enrichments of light REE probably introduced by metasomatism. (b) PGE, Re and Au for the same rocks. Elements are arranged in the order of decreasing melting points. Sources of data: Metals: this work; REE: Kurat et al. (1993); CI-normalizing values: Palme and Beer (1993).

lite Z-13 is depleted in heavy rare earth elements (HREE) with $\sim 1.4 \times$ CI, compared to Z-14 and Z-34. The amphibolite–harzburgite (Z-17) belongs to the group of *depleted peridotites*. The rock is enriched in LREE ($2 \times$ CI) and strongly depleted in the HREE ($0.3 \times$ CI). Z-36 is a *metasomatized peridotite* and shows evidence of modal metasomatic alteration by the growth of porphyroblasts of amphibole.

The major and trace element composition of these five samples is consistent with an origin as residues of partial melting of primitive upper mantle, as shown by Kurat et al. (1993). These rocks fit worldwide trends in plots of CaO, Al_2O_3, Sc, Ni, etc., vs. MgO (see also O'Neill and Palme, 1998).The two samples Z-31, an orthopyroxenite and Z-25, a plagioclase wehrlite have a more complex origin, as is apparent from their bulk compositions. Rocks, such as Z-31, are present as cm to m wide dikes. Their grain size is very large (5–10 cm). Sample Z-26 has high CaO and low MgO-contents, reflecting a high modal clinopyroxene content (Kurat et al., 1993). A more detailed sample description is given in Appendix A.

3. Sample preparation and analytical procedures

Whole rock samples (50 g) were crushed with a polyethylene-wrapped hammer into < 1 cm pieces, which were then ground in an agate mill to a grain size below 50 μm. Aliquots of 10 g of homogenized samples were used for analysis. The HSE were analyzed by a slightly modified version of the fire assay neutron activation method, using nickel sulfide as collector following the analytical procedures for large samples (25 to 50 g) described by Robert et al. (1971; Robert et al., 1975), Hoffman et al. (1978), and Robert (1987). Earlier studies by Schmidt and Pernicka (1994) had shown that the PGE, Re and Au partition strongly into Ni-sulfide liquid in equilibrium with a silicate melt. The fraction of HSE in the silicate melt, under equilibrium conditions, is below 1%, in all cases. Experimentally determined partition coefficients between Fe-sulfide and silicate melts range from 10^3 to 10^5, as reported in the literature (e.g., Stone et al., 1990; Fleet et al., 1991; Bezmen et al., 1994).

The fire-assay charges consisted of 2 g nickel, 1.4 g sulfur, 5 g Na_2CO_3, 5 g $Li_2B_4O_7$ and 10 g rock sample. The flux mixture, collector and sample were mixed thoroughly and transferred into a fire clay crucible which was covered with a clay lid. The fusion was carried out at 1050°C for 1 h in a muffle furnace. After cooling, the crucible was destroyed and the Ni-sulfide button was separated from the slag. The button was than heated (3 h) on a hot plate (80 ± 10°C) in a covered beaker with concentrated hydrochloric acid, and the solution was filtered (pore size 0.45 μm) to obtain the insoluble PGE, Re and Au. The precipitate was washed first with de-ionized water, then with ethanol and left to dry. Finally, the filter paper was folded, sealed in polyethylene containers and analyzed by INAA. Multi-element standards were prepared from main stock standard solutions.

4. Neutron activation

The INAA procedure involved two irradiations: a short irradiation for Rh and a long irradiation for the other elements. Samples were first placed in a polycarbonate rabbit and irradiated for 5 min at a thermal neutron flux of 1.7×10^{12} n cm^{-2} s^{-1} in the RP1 hydraulic rabbit facility of the Mainz TRIGA Reactor. For the short irradiation times, sample and standard were put together in one capsule. After a delay time of 2 min, samples were counted for 500 s. The ^{104m}Rh ($T_{1/2} = 4.41$ min) γ-peak at 51 keV was used for the Rh-determination. A Rh standard was measured for 3 min in the same counting position as the sample.

After completion of the first irradiation, samples were sealed together with prepared chemical standards into a clean capsule (21 mm $\times$ 53 mm) and irradiated for 12 h in the core of the reactor at a flux of 4×10^{12} n cm^{-2} s^{-1}. After a decay time of 16 h, γ-spectra of the samples and standards were measured to determine Pd as ^{109}Pd ($T_{1/2} = 13.43$ h), Re as ^{188}Re ($T_{1/2} = 16.98$ h), Pt as ^{199}Au ($T_{1/2} = 3.14$ d), Au as ^{198}Au ($T_{1/2} = 2.7$ d), Ir as ^{192}Ir ($T_{1/2} = 73.8$ d), Os as O_s^{191} ($T_{1/2} = 15.4$ d), and Ru as ^{103}Ru ($T_{1/2} = 39.4$ d) with γ-ray energies of 88, 155, 158, 411, 468, 129 and 479 keV, respectively. Analyses were performed with a Ge(Li) detector (Ortec, FWHM = 1.69 keV at 1.332 MeV and 0.69 keV at 122 keV, respectively). All γ-spectra were analyzed using an updated version of the INTER-GAMMA program (Intertechnique Deutschland, Mainz). Because of the contribution of ^{195m}Pt ($T_{1/2} = 4.02$ d) to the O_s^{191} ($T_{1/2} = 15.4$ d) peak at 129 keV, all Os values were corrected accordingly.

Sulfur data were obtained on aliquots of the powdered samples by Dreibus with a carbon and sulfur analyser (Dreibus et al., 1995). The Cu data were obtained by ICP at the institute of mineralogy and geochemistry, University of Cologne, using certified standard rocks as standards. The Cu analyses were, 1 year after first Cu-analyses, repeated on aliquots and the results were within 5% identical to the original data.

5. Results

The bulk chemical data obtained by Kurat et al. (1993) are given in Table 1. Included in this Table are the results of the S and Cu analyses. Concentrations of Os, Re, Ir, Ru, Rh, Pd, and Au in the Zabargad rocks are given in Table 2. Analytical uncertainties ($\pm 1\sigma$) reflect the propagation of errors due to counting statistics and include uncertainties of elemental abundances in the reagents. Precisions estimated from counting statistics corresponding to one

Table 2
Rh, Pd, Os, Ir, Ru, Au and Re of harzburgite (Z17), dunite (Z36), lherzolite (Z13, Z14 and Z34), pyroxenite (Z31) and wherlite (Z26) from Zabargad Island, Red Sea, and in reference samples (WGB-1, UMT-1, WPR-1), by NiS fire assay and INAA
Method detection limits are defined as background plus 3 standard deviations; n.d. = not determined. Unaccounted for uncertainties might include absolute variations due to the yield of the NiS fire assay plus acid dissolution and filtering, and sample inhomogeneity. We estimate the true uncertainty at 7–10% for absolute concentrations (see McDonald et al., 1994) and 4–5% for interelement ratios.

Rock type	Rh (ng/g)	Pd (ng/g)	Os (ng/g)	Ir (ng/g)	Ru (ng/g)	Au (ng/g)	Re (pg/g)
Z-17 Amp-harz	0.69 ± 0.07	5.7 ± 0.3	1.78 ± 0.04	1.98 ± 0.03	3.6 ± 0.1	0.41 ± 0.20	214 ± 25
Z-36 Amp-duni	1.28 ± 0.10	5.2 ± 0.8	2.83 ± 0.10	3.10 ± 0.03	5.4 ± 0.4	1.30 ± 0.20	< 90
Z-13 Sp-lher	1.02 ± 0.03	7.0 ± 0.2	2.87 ± 0.08	2.99 ± 0.03	5.2 ± 0.4	1.33 ± 0.2	205 ± 12
Z-34 Sp-pl-lher	0.86 ± 0.08	8.8 ± 2.7	1.84 ± 0.04	1.69 ± 0.03	3.2 ± 0.1	0.45 ± 0.20	230 ± 37
Z-14 Sp-pl-lher	1.99 ± 0.08	7.8 ± 0.5	3.48 ± 0.24	3.28 ± 0.03	5.7 ± 0.3	1.16 ± 0.20	289 ± 38
Z-31 Opx-pyro	2.38 ± 0.07	9.3 ± 0.7	10.22 ± 0.22	7.90 ± 0.03	14.6 ± 0.5	0.99 ± 0.20	< 90
Z-26 Pl-wher	9.85 ± 0.20	84.5 ± 1.7	56.19 ± 0.69	29.08 ± 0.05	53.3 ± 1.0	6.31 ± 0.20	< 180
Blank	< 0.25	< 0.5	< 0.2	0.19 ± 0.03	< 0.4	0.4 ± 0.2	< 20
WGB-1[1]	0.32[a]	13.9 ± 2.1	n.d.	0.33[a]	0.3[b]	2.9 ± 1.1	n.d.
WGB-1[1a]	n.d.	11.7 ± 2.4	n.d.	n.d.	n.d.	1.50 ± 0.71	n.d.
WGB-1[2a]	0.52 ± 0.07	13.3 ± 0.9	< 0.5	0.20 ± 0.03	0.8 ± 0.2	2.03 ± 0.20	270 ± 20
WGB-1[2b]	0.28 ± 0.07	14.7 ± 0.7	0.2 ± 0.1	0.04 ± 0.03	< 0.4	0.70 ± 0.20	596 ± 10
WGB-1[2c]	0.39 ± 0.06	11.2 ± 0.1	0.43 ± 0.02	0.22 ± 0.01	< 0.3	0.78 ± 0.20	590 ± 10
WGB-1[2d]	0.36 ± 0.04	11.0 ± 0.1	0.44 ± 0.02	0.22 ± 0.01	< 0.3	0.47 ± 0.20	640 ± 10
WGB-1[2e]	0.16	12.6	n.d.	0.22	0.26	2.1	n.d.
WGB-1[2f]	< 0.5	10.9 ± 2.2	n.d.	3.3 ± 0.2	4.6 ± 1.4	n.d.	n.d.
UMT-1[3]	9.5 ± 1.1	106 ± 3	8.0[a]	8.8 ± 0.6	10.9 ± 1.5	48 ± 2	3000[b]
UMT-1[3a]	n.d.	104 ± 10	n.d.	n.d.	n.d.	46.2 ± 5.3	n.d.
UMT-1[2a]	7.57 ± 0.11	98.0 ± 2.0	6.0 ± 0.3	7.31 ± 0.10	8.2 ± 1.0	27.0 ± 0.5	n.d.
UMT-1[2b]	9.87 ± 0.20	93.0 ± 2.0	7.2 ± 0.3	7.82 ± 0.10	9.6 ± 0.5	32.6 ± 0.2	2999 ± 25
UMT-1[2f]	9.5 ± 0.7	98.8 ± 5.0	n.d.	9.7 ± 1.0	11.1 ± 2.1	n.d.	n.d.
WPR-1[4]	13.4 ± 0.9	235 ± 9	13[a]	13.5 ± 1.8	22 ± 4	42 ± 3	n.d.
WPR-1[4a]	13.3 ± 0.4	232 ± 6	16.8 ± 0.6	12.8 ± 0.2	19.4 ± 1.2	16.2 ± 0.5	5000 ± 100
WPR-1[4b]	12.1 ± 0.3	226 ± 5	17.1 ± 0.5	13.2 ± 0.2	19.7 ± 1.2	19.1 ± 0.5	4200 ± 100
WPR-1[4c]	n.d.	n.d.	n.d.	16.4 ± 1.0	n.d.	36.0 ± 1.1	n.d.
WPR-1[4d]	n.d.	n.d.	n.d.	18.7 ± 1.1	n.d.	36.0 ± 1.1	n.d.
WPR-1[4e]	13.1 ± 0.7	223 ± 10	n.d.	13.4 ± 0.7	19.8 ± 1.2	45.1 ± 5.0	n.d.
WPR-1[4f]	n.d.	223	n.d.	13.1	20	n.d.	n.d.
CI-chondrite[5]	140 ± 4	556 ± 56	486 ± 24	459 ± 14	714 ± 71	152 ± 8	38300 ± 2681

Table 3
Comparison of results obtained by Kurat et al. (1993) by INAA on small samples (about 200 mg) and by nickel sulphide fire-assay and INAA on large samples (10 g) from this work
n.d. = not determined.

Rock type	Ir[a] (ng/g)	Ir[b] (ng/g)	Au[a] (ng/g)	Au[b] (ng/g)
Z-17 Amp-harz	1.98 ± 0.03	5.5 ± 0.8	0.41 ± 0.20	0.6 ± 0.1
Z-36 Amp-duni	3.10 ± 0.03	4.6 ± 0.7	1.30 ± 0.20	1.1 ± 0.2
Z-13 Sp-lher	2.99 ± 0.03	5.6 ± 0.8	1.33 ± 0.20	1.4 ± 0.2
Z-34 Sp-pl-lher	1.69 ± 0.03	4.1 ± 0.6	0.45 ± 0.20	n.d.
Z-14 Sp-pl-lher	3.28 ± 0.03	3.8 ± 0.6	1.16 ± 0.20	n.d.
Z-31 Opx-pyro	7.90 ± 0.03	5.3 ± 0.8	0.99 ± 0.20	n.d.
Z-26 Pl-wher	29.08 ± 0.05	28.0 ± 4.2	6.31 ± 0.20	9.0 ± 1.4

[a] This work.
[b] Kurat et al. (1993).

standard deviation for the analyzed elements are: Os ± 10%; Re ± 10%; Ir ± 1%; Ru ± 5%; Rh ± 10%; Pd ± 5%; and Au ± 1%. Upper limits (3σ) are shown for abundances below detection limits. For a typical sample size of 10 g, total blanks correspond to <2, <0.2, 1.9 ± 0.3, <4, 2.5, <5, and 4 ± 2 ng Os, Re, Ir, Ru, Rh, Pd and Au, respectively. Detection limits are defined as background plus three standard deviations. Except for Pt, Au and Ir, reagent blanks of the PGE were below detection limits. For Pt unusually high blank values were found. Therefore, the Pt results could not be used in this work. Iridium and Au concentrations have been corrected for blank values in Table 2.

Schmidt and Pernicka (1994) showed that Re is quantitatively extracted with PGE into NiS, allowing the determination of Re together with PGE in a single sample (Schmidt and Pernicka, 1990). Generally, any loss of an element analyzed for is estimated to be below 5% (dissolution plus sealing in small polyethylene capsules). However, if losses occur, they primarily affect the absolute level of PGE; ratios among them remain constant.

The accuracy of the method was determined by analyzing 2 g aliquots of certified reference materials by Schmidt (1997). In Table 2 we also report results of three standard reference materials, one low-level standard WGB-1 (gabbro), one petidotite standard (WPR-1) and one ultramafic ore tailing standard UMT-1 delivered by CANMET (see also Snow and Schmidt, 1998a), Department of Energy, Mines and Resources, Canada. In comparison, the recommended values and literature data (Hall and Pelchat, 1994) for the mean and standard deviation for the

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Notes to Table 2:
[1] Gabbro rock WGB-1 PGE reference material, CANMET (1994a), [a] provisional, [b] information.
[1a,3a] Hall and Pelchat (1994); inductively coupled plasma mass spectrometry (ICP-MS).
[2a–d] This work; see also Snow and Schmidt (1998a). Four analysis of certified reference material WGB-1 on 10 g (2a–d). Pt concentrations for (2c) and (2d) are 6.0 ± 0.4 ng/g and 5.9 ± 0.2 ng/g, respectively.
[2e] Pattou et al. (1996); NiS/ICP-MS.
[2f] Paukert and Rubeska (1993); graphite furnace atomic absorption spectrometry.
[3] Ultramafic ore tailings UMT-1 PGE reference material, CANMET (1994b).
[4] Altered peridotite PGE reference material, CANMET (1994c).
[4a,b] This work; replicate analysis of certified reference material WPR-1 on 3.07 g (4a) and 5.31 g (4b). Pt concentrations for (4a) and 4b) are 245 ± 10 ng/g and 243 ± 8 ng/g, respectively.
[4c–d] Replicate instrumental neutron activation analysis of certified reference material WPR-1 on 115 mg (4c) and 141 mg (4d) by B. Spettel (MPI for Chemistry, Mainz).
[4e] ICP-MS after hydrolytic extraction by Gueddari et al. (1996).
[4f] ICP-MS after hydrolytic extraction by Barratt et al. (1997).
[5] Data are from Palme and Beer (1993), except Rh (Jochum, 1996).

reference material and double analysis from this work are given in Table 2. The concentration of Au in UMT-1 found here is only 56–69% of the recommended value. It is possible that Au is heterogeneously distributed in UMT-1, as the Au content found for WGB-1^{2c} is in reasonable agreement with literature data (1.50 ± 0.71 ng/g; see Hall and Pelchat, 1994). Hall and Pelchat (1994) noted heterogeneous distribution of Au in well homogenized samples.

Comparison of results for the analyzed samples obtained with INAA on smaller samples (about 200 mg) by Kurat et al. (1993) and from this work indicate a somewhat inhomogeneous distribution of Ir (and possibly Os, Ru, Pd, Rh, and Re) in these rocks (Table 3). In contrast to Ir, Au seems to be more homogeneously distributed in Zabargad rocks, as can be seen from Table 3. Inhomogeneous distribution of PGE, Re and Au is not uncommon. Luck and Allègre (1991) reported significant variations of

Table 4
Average contents of highly siderophile elements (ng/g) of massive peridotites, xenoliths and abyssal peridotites (oceanic mantle) from different localities (literature data) in comparison with data from Zabargad
n.d. = not detected. HSE in ng/g.
Lherzolite massifs: (1a) Baldissero, (1b) Balmuccia, (1c) Finero (Western Italian Alps); (2) Eastern Central Alps; (3) Ronda; (4) Pyrenean; (5a–e) Zabargard (Red Sea); (6) Ronda and Beni Bousera; (7) Ligurides (Northern Apennines).
Xenoliths: (8) Nunivak Island, AK; Kilbourne Ilole, NM; San Carlos, AZ; Cochise crater, AZ; Salt Lake Crater, HI; San Quintin, Mexico; Mt. Quincan, Australia; Matsoku, Lesotho. (9) Mt. Porndon, Victoria and Kilbourne Ilole, New Nexico; (10) South Africa. (11a) Montbriancon, (11b) Montferrier (Massif Central, France); (12) Cameroon Line.
Oceanic mantle: (13) Atlantic, Pacific and Indian oceans.

Locality	Rh	Pd	Os	Ir	Ru	Au	Re	Number of samples	Ref.
Massive peridotites									
(1a)	1.0 ± 1.0	7.6 ± 3.2	n.d.	n.d.	n.d.	2.7 ± 1.3	n.d.	8	(a)
(1b)	1.0 ± 0.9	6.5 ± 2.2	n.d.	n.d.	n.d.	2.7 ± 1.8	n.d.	8	(a)
(1c)	0.2 ± 0.1	1.8 ± 1.2	n.d.	n.d.	n.d.	2.9 ± 3.0	n.d.	7	(a)
(2)	n.d.	6.4 ± 1.7	3.4 ± 1.3	3.3 ± 2.2	8.2 ± 3.4	n.d.	n.d.	22	(b)
(3)	n.d.	n.d.	4.6 ± 2.1	n.d.	n.d.	n.d.	0.37 ± 0.35	12	(c)
(4)	1.07 ± 0.19	5.5 ± 1.5	n.d.	3.19 ± 0.63	6.65 ± 2.25	1.0 ± 0.4	n.d.	14	(d)
(5a)	n.d.	6.7 ± 1.8	n.d.	2.7 ± 0.7	n.d.	0.8 ± 1.0	n.d.	8	(c)
(5b)	n.d.	n.d.	4.27 ± 0.37	n.d.	n.d.	n.d.	n.d.	2	(f)
(5c)	n.d.	n.d.	n.d.	4.43 ± 0.32	n.d.	1.4 ± 0.2	n.d.	7	(g)
(5d)	n.d.	n.d.	4.62 ± 0.42	n.d.	n.d.	n.d.	0.322 ± 0.013	2	(h)
(5e)	1.29 ± 0.61	7.4 ± 0.4	2.73 ± 0.83	2.65 ± 0.85	4.7 ± 1.3	0.98 ± 0.47	0.24 ± 0.04	3	(i)
(6)	1.66 ± 0.66	4.89 ± 1.28	n.d.	2.21 ± 0.50	6.32 ± 1.18	3.37 ± 3.43	n.d.	10	(j)
(7)	1.21 ± 0.38	4.93 ± 1.13	2.51 ± 0.28	2.71 ± 0.29	5.32 ± 0.52	3.88 ± 2.11	0.16 ± 0.05	15	(k)
Xenoliths									
(8)	n.d.	4.5 ± 2.7	3.8 ± 2.4	4.2 ± 2.6	n.d.	0.78 ± 0.74	0.108 ± 0.080	19	(l)
(9)	n.d.	4.6 ± 3.3	n.d.	3.6 ± 2.5	n.d.	0.7 ± 0.4	n.d.	6	(m)
(10)	n.d.	n.d.	4.0 ± 2.9	n.d.	n.d.	n.d.	n.d.	12	(n)
(11a)	0.92 ± 0.26	3.5 ± 1.6	n.d.	3.0 ± 0.7	5.3 ± 1.4	0.6 ± 0.4	n.d.	8	(o)
(11b)	1.27 ± 0.40	5.6 ± 1.4	n.d.	3.7 ± 1.3	6.4 ± 1.5	1.70 ± 0.63	n.d.	4	(o)
(12)	n.d.	2.48 ± 1.03	n.d.	2.46 ± 1.23	4.29 ± 2.14	n.d.	n.d.	6	(p)
Oceanic mantle									
(13)	1.16 ± 0.22	4.90 ± 1.99	2.70 ± 0.68	2.62 ± 0.74	5.30 ± 1.52	0.59 ± 0.37	0.10 ± 0.05	9	(q)

(a) Garuti et al. (1984); (b) Schmidt (1991); (c) Reisberg et al. (1991); (d) Pattou et al. (1996); (e) Hamlyn et al. (1985); (f) Martin (1991); (g) Spettel et al. (1991); (h) Brueckner et al. (1995); (i) this work; (j) Gueddari et al. (1996); (k) Snow et al. (1998); (l) Morgan et al. (1981); (m) Mitchell and Keays (1981); (n) Walker et al. (1989); (o) Lorand and Pattou (1996); (p) Rehkämper et al. (1997); (q) Snow and Schmidt (1998a).

Re and Os in ultramafic rocks and Birck and Allègre (1994) noted variations in Os by a factor of two in powdered samples of eucrites and lunar basalts.

6. Comparison with literature data

The range in Ir and Pd concentrations of the Zabargad peridotites with upper mantle chemistry analyzed here (Ir from 1.98 to 3.28 ppb and Pd from 5.7 to 9.3 ppb) is similar to the range of Ir (3.0 ± 0.9 ng/g, $N = 5$) and Pd (5.8 ± 1.7 ng/g, $N = 5$) in LREE-depleted spinel lherzolites and of Ir (3.1 ± 2.3 ng/g, $N = 3$) and Pd (7.5 ± 1.0 ng/g, $N = 3$) in LREE-enriched hornblende peridotite from Zabargad found by Hamlyn et al. (1985). Spettel et al. (1991) reported for peridotites from Zabargad Ir and Au contents of 4.43 ± 0.32 ng/g and 1.4 ± 0.2 ng/g, respectively (see also Tables 3 and 4).

A comparison of the Zabargad HSE data with average concentrations of HSE in upper mantle rocks from other localities is given in Table 4. The average HSE concentrations in the Zabargad rocks are similar to concentrations reported for other upper mantle rocks, including recent data for oceanic peridotites (Snow and Schmidt, 1998b). The total variation in Rh concentrations are only from 1 to 1.66 ng/g, except for low Rh contents (0.2 ng/g) in samples from Finero reported by Garuti et al. (1984). The spread in average Os and Ir concentrations is less than a factor of two, from 2.73 to 4.62 for ng/g for Os and from 2.21 to 4.43 ng/g for Ir, respectively. Similar variations are seen for Ru (4.2 to 7.8 ng/g). Only Pd and Au show a somewhat larger spread, from 1.8 to 7.6 ng/g for Pd and from 0.6 to 2.9 ng/g for Au). The Re data cluster at about 0.3 ng/g except for lower contents in the abyssal peridotites.

7. Discussion

7.1. Major and trace element composition (except PGE)

The bulk compositions (Table 1) of five samples Z-13, Z-14, Z-34 (primitive peridotites), Z-17 (depleted peridotite) and Z-36 (metasomatized peridotite) follow chemical trends established by a large number of upper mantle rocks, including xenoliths and massive peridotites (Jagoutz et al., 1979; Palme and Nickel, 1985; McDonough and Sun, 1995; O'Neill and Palme, 1988). The MgO contents range from 38.14% to 44.17% while Al_2O_3-contents decrease from 3.64% to 0.98%. These trends are qualitatively understood in terms of removal of increasing amounts of partial melts from undepleted, primitive mantle. The two samples with lowest Al_2O_3 and TiO_2 contents, have unusual REE-patterns (Fig. 1a). The metasomatized peridotite (Z-36) has extreme enrichments of the light REE. The REE pattern of the depleted peridotite (Z-17) is approximately parallel to that of Z-36 but has more than a factor of 10 lower absolute abundances of REE (Fig. 1). Apparently major and trace elements of these two samples are decoupled.

Two of the samples Z-26 and Z-31 have MgO contents (23.46 and 31.12%) and Al_2O_3 contents (5.86 and 5.17%), far outside trends for upper mantle rocks. As discussed below these two samples also have unusually high contents of HSEs. The bulk composition of sample Z-31 is typical of a pyroxene-dominated rock, with high Sc, Cr, and Mn and low Co and Ni contents (Table 1). Abundances of the HREE (Fig. 1a) are at 2 × CI, but La is much less abundant (0.35 × CI).

The S and Cu concentrations of the samples analyzed (Table 1) show correlations with neither major element chemistry nor with trace elements. Also, there is no correlation between Cu and S (Fig. 2). The Zabargad samples analyzed here have S concentrations comparable to those of other orogenic lherzolites and significantly above the S contents of peridotitic xenoliths (Fig. 2). However, the Zabargad samples do not show the correspondingly high Cu contents that are often found in samples of massive lherzolites (Fig. 2). This may reflect loss of Cu through extensive metasomatism. The two samples with the lowest Cu contents are the depleted perodotite (Z-17) and the metasomatized peridotite (Z-36), both samples have very unusual REE pattern as described above.

7.2. The PGE signature of Zabargad rocks

The PGE patterns in the Earth are often compared with meteorite patterns that are in many cases thought

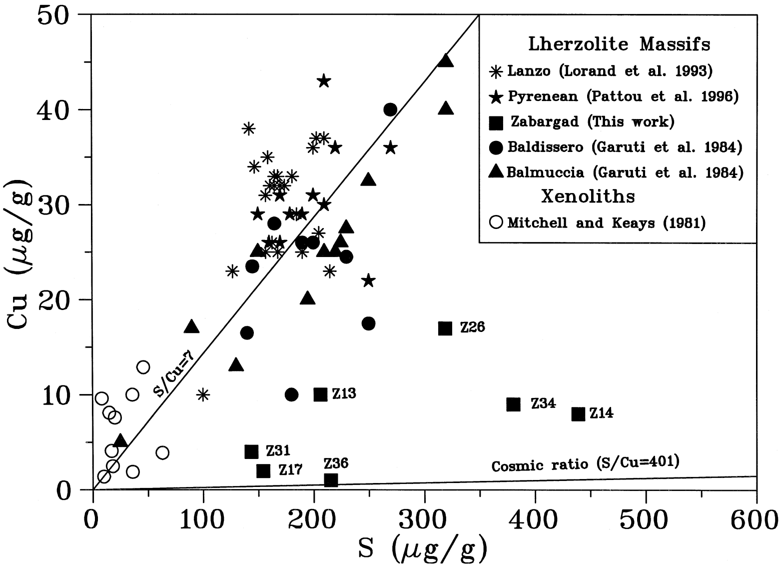

Fig. 2. Cu vs. S from Zabargad rocks (this work) compared with literature data. Xenoliths have, in general, low S and low Cu contents and massive peridotites are high in S and Cu. Zabargad rocks are unusual with high S but low Cu.

to reflect the primordial abundances of the solar system. The type one carbonaceous chondrites (CI) represent surprisingly well the elemental abundances of the average solar system; CI-chondrite abundances match solar photospheric abundances within 10% for most elements heavier than oxygen and except rare gases (Palme and Beer, 1993). Variations in PGE ratios among different types of chondrites are comparatively small, smaller than the deviations from chondritic meteorites discussed here. For example, data by Meisel et al. (1996) give an average Os/Re ratio of 12.40 ± 0.28 (5 samples) for carbonaceous chondrites, 11.11 ± 0.48 (15 samples) for ordinary chondrites and 11.43 ± 0.43 (10 samples) for enstatite chondrites. Similarly uniform Os/Ir ratios are found in different types of chondritic meteorites. The average Os/Ir ratio listed by Wasson and Kallemeyn (1988) is 1.05. There may be slightly higher ratios in enstatite chondrites as shown by the data of Hertogen et al. (1983) with 1.15 ± 0.01, while Morgan (1985) found an average H-chondrite ratio of 0.99 ± 0.06 (10 meteorites).

For Ru, Pt and in particular Rh, there are fewer data, consequently interelement ratios are not so well defined, but the available evidence suggests that ratios are constant within about $\pm 10\%$ in various groups of chondritic meteorites, similar to what is found for Ir, Os and Re.

Ratios of refractory metals to non-refractory metals are variable in chondritic meteorites. This is, for example, visible in the significant variations of Pd/Ir-ratios in chondritic meteorites. Enstatite chondrites are lowest in refractory elements and therefore have the highest Pd/Ir-ratios. Data by Hertogen et al. (1983) for enstatite chondrites suggest an average Pd/Ir ratio of 1.32 ± 0.20 with a range from 1.08 to 1.68 compared to a CI-value of 1.16 (Palme and Beer (1993). Morgan (1985) found an average Pd/Ir ratio of 1.01 ± 0.9 for 10 ordinary chondrites. The depletion of refractory siderophile elements in enstatite chondrites is thus significantly less than the corresponding depletion of refractory lithophile elements (factor of two). As will be seen below these variations are small compared to variations reported in upper mantle rocks.

7.2.1. Ir, Os and Ru

In Fig. 1b, chondrite normalized abundances of the HSE are plotted in order of decreasing melting points of the metals (Os, Re, Ir, Ru, Rh, Pd, Au). Analytical uncertainties are in most cases smaller than symbol sizes. All samples have, except for Pd, Re and Au, roughly (i.e., within a factor of two) flat CI-normalized patterns despite variations in absolute abundances by a factor of 10. The large variations in absolute abundances are primarily produced by the two unusual samples, the plagioclase wehrlite Z-26 and the orthopyroxenite Z-31. The total variation in Ir of the five ‘‘normal’’ samples is less than a factor of two. With an average Ir content of 2.61 ± 0.36 ppb they are at the lower end of typical upper mantle rocks (e.g., Morgan et al., 1981; Spettel et al., 1991). The two anomalous samples, Z-26 and Z-31, with Ir contents of 29.08 ppb and 7.9 ppb, respectively, have, however, nearly flat CI-normalized abundance patterns, similar to the patterns observed for the other samples (Fig. 1b), except for low Re and an extra enhancement of Pd and to a lesser extent of Os in Z-26. Apparently the PGE were transported within the mantle as a single component (see below). The element Os is, in the solar nebula environment, as refractory as Ir (Palme and Wlotzka, 1976). Both elements should therefore occur in chondritic ratios in the bulk Earth and, if the PGE were delivered to the Earth’s mantle with a chondritic component, also in the Earth’s mantle. The Os/Ir ratio in Zabargad rocks is, indeed, chondritic within error limits. From Table 1, a mean Os/Ir ratio of 1.16 ± 0.15 (standard deviation of the mean) is calculated, compared to the CI-ratio of 1.06. Excluding the unusual sample Z-26 (Os/Ir of 1.93) from the average yields a ratio of 1.04 ± 0.07, even closer to the CI-ratio. Chondritic Os/Ir ratios in mantle rocks were also reported by Morgan et al. (1981) in a suite of 19 spinel and garnet lherzolitic xenoliths (mean Os/Ir ratio of 0.94 ± 0.06). From the present data base of mantle rocks, one may infer a chondritic Os/Ir-ratio of the upper mantle to within ±5%. Until recent Re–Os studies there were comparatively few Os-analyses reported in the literature, primarily because of the poor sensitivity of Os for neutron activation analysis. This has now changed. However, there are still few Os-Ir data for the same samples.

A chondritic Os/Ir ratio in the Earth’s mantle should also imply chondritic Ru/Os and Ru/Ir ratios, as Ru is similarly refractory as Ir, and Ru and Os are chemically similar elements. The mean Ru/Ir-ratio of the analyzed Zabargad rocks is 1.80 ± 0.03. This is 15% above the CI-chondritic value of 1.56. A mean Ru/Ir ratio of 14 Pyrenaen spinel lherzolites gave a value of 1.97 ± 0.11 slightly higher than the Zabargad ratio reported here, but nearly indistinguishable within error limits (Pattou et al., 1996). An average Ru/Ir ratio of 2.00 ± 0.10 is calculated from a recent data set of nine oceanic peridotites (Snow and Schmidt, 1998a) and a ratio of 1.97 ± 0.14 was determined for 15 Ligurian peridotite samples (Snow et al., 1998). New data from relatively fertile xenoliths (CaO from 3.0 to 3.38%) from the Cameroon Line gave an average Ru/Ir ratio of 1.74 ± 0.13, while depleted xenoliths from Northern Tanzania (CaO from 0.14 to 0.72%) had significantly lower PGE contents with much more variable Ru/Ir ratios, higher and lower than CI (Rehkämper et al., 1997). Five analyses of spinel lherzolites from Alligator Lake (Evans et al., 1993) also show an enhanced Ru/Ir ratio (2.6 ± 0.48) compared to the chondritic ratio (Fig. 3). There appears to be a worldwide trend in upper mantle rocks for higher than chondritic Ru/Ir ratios, at least for fertile mantle samples. The significance of these trends will be discussed below.

From the data of the three refractory siderophile elements Os, Ir and Ru we conclude: (1) The Os/Ir ratios are, within 10 to 20% chondritic and secondary processes that have affected some Zabargad rocks did not alter this ratio in any of the analyzed rocks. This is in agreement with the results of many other studies of mantle rocks. (2) Relative to CI-chondrites there is 20 to 40% enhancement of Ru in mantle rocks from Zabargad and also in other (fertile) upper mantle rocks. The enhancement of Ru is very clear from the CI-normalized element plot (Fig. 4).

Further careful analyses are required to see if the overabundance of Ru in Zabargad is representative of the upper mantle or if this is only a local phenomenon. The Pattou et al. (1996) data, the oceanic data (Snow and Schmidt, 1998a) and the recent Rehkämper et al. (1997) data suggest, as mentioned above, that high Ru/Ir ratios are widespread and may be characteristic of a larger fraction, if not for the whole of the upper mantle.

7.2.2. Re

Under reducing conditions Re is one of the most refractory metals, cosmochemically related to Ir, Os and Ru (Palme and Wlotzka, 1976). In refractory metal alloys Re is slightly less resistant to oxidation

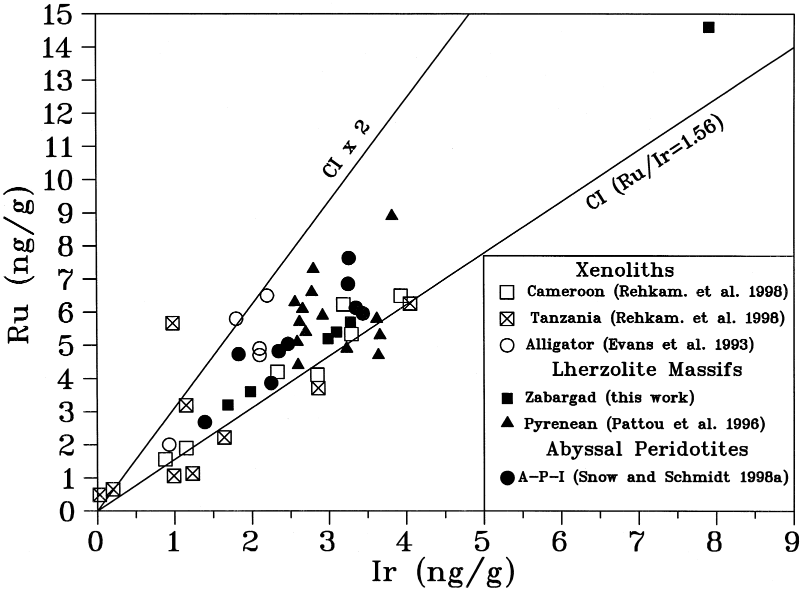

Fig. 3. Ru vs. Ir from Zabargad rocks (this work) compared with literature data. The CI-chondrite ratio is indicated. There is a clearly resolvable enrichment in upper mantle Ru/Ir ratios, compared to CI-chondrites.

than Os (Palme et al., 1998). In addition, Re is moderately incompatible with residual mantle phases during partial melting, in contrast to the three elements discussed above. This leads to high Re/Os ratios in mantle melts and thus in the crust, whereas residual upper mantle rocks commonly have complementary, i.e., low Re/Ir ratios, depending on the extent of depletion. Only two samples of the UM-

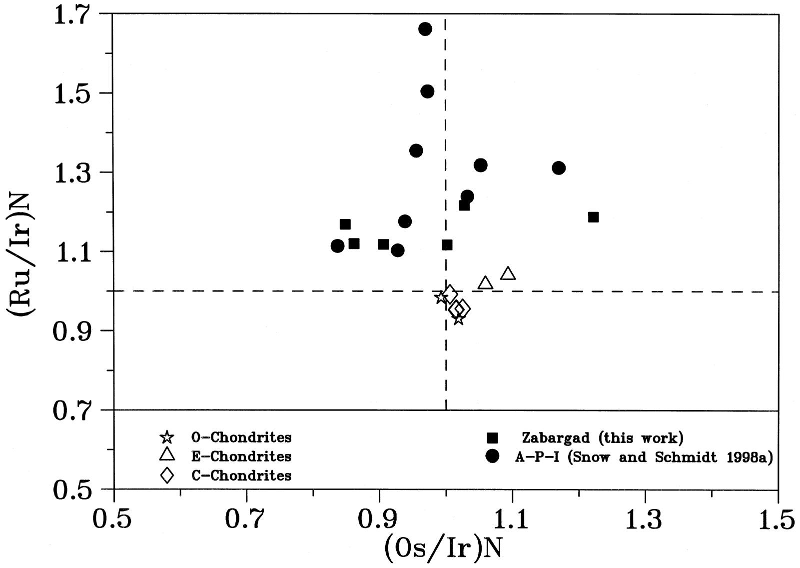

Fig. 4. CI-normalized Ru/Ir vs. Os/Ir ratios. Upper mantle rocks have higher than CI-chondritic Ru/Ir ratios but, on average, chondritic Os/Ir ratios (see text). Chondrite data from Wasson and Kallemeyn (1988).

reference suite of 18 xenoliths with high Ir (Basaltic Volcanism Study Project, 1981; Morgan et al., 1981) have approximately chondritic Re/Ir ratios, all others have lower ratios (Fig. 5). These two samples have the lowest MgO contents of the suite and thus represent comparatively fertile mantle. All other xenoliths are depleted in Re and the extent of depletion correlates roughly with increasing MgO or decreasing Al_2O_3 (Morgan et al., 1981; Morgan, 1986), reaching Re/Ir ratios as low as 0.002 for UM-10 with a MgO content of 44.13% (Basaltic Volcanism Study Project, 1981). The isotopic composition of Os in upper mantle rocks is consistent with the depletion of Re by partial melting. Reisberg and Lorand (1995) showed for a suite of Pyrenean spinel–lherzolites that when replacing Re by Al_2O_3 an improved correlation with $^{187}Os/^{188}Os$ is obtained and a formal age of a single mantle melting event may be estimated. The larger scatter of Re, or, in other words, the lack of a correlation of Re with Al_2O_3 is ascribed to recent Re mobilization. A similar situation is found for the Zabargad rocks analyzed here. There is no good correlation between Re/Os vs. Al_2O_3, even when discarding the two unusual samples Z-31 and Z-26. The most depleted sample Z-17 has the highest Re content (Fig. 6). However, the low $^{187}Os/^{188}Os$ ratio found for this rock is consistent with the low Al_2O_3 of this sample (Snow and Schmidt, 1998b), indicating recent addition of Re.

The two samples with enriched PGE (Fig. 1b) document the high mobility of a probably S-rich component acting as a carrier phase for PGE (see below). Both samples are, however, depleted in Re. Either Re was never part of the PGE-rich sulfides or it was later lost from the sulfides through weathering. The correlation of $^{187}Os/^{188}Os$ with Al_2O_3 found in Zabargad and observed in the Pyrenaen lherzolites (Reisberg and Lorand, 1995) suggests a behavior of Re similar to that of Al_2O_3, but different from the other PGE, such as Ir or Os. Rhenium may thus have a different host phase from the other PGE. This conclusion is confirmed by findings of Burton et al. (1998). These authors have recently studied the distribution of Re and Os in mantle rocks and concluded that Os is largely concentrated in sulfide and Re in silicates.

7.2.3. Rh, Pd and Au

The element Rh is rarely analyzed in upper mantle rocks. It is, relative to Ir, slightly enriched in Zabargad rocks, as reflected in the average Rh/Ir ratio of 0.39 ± 0.04 and compared to the chondritic

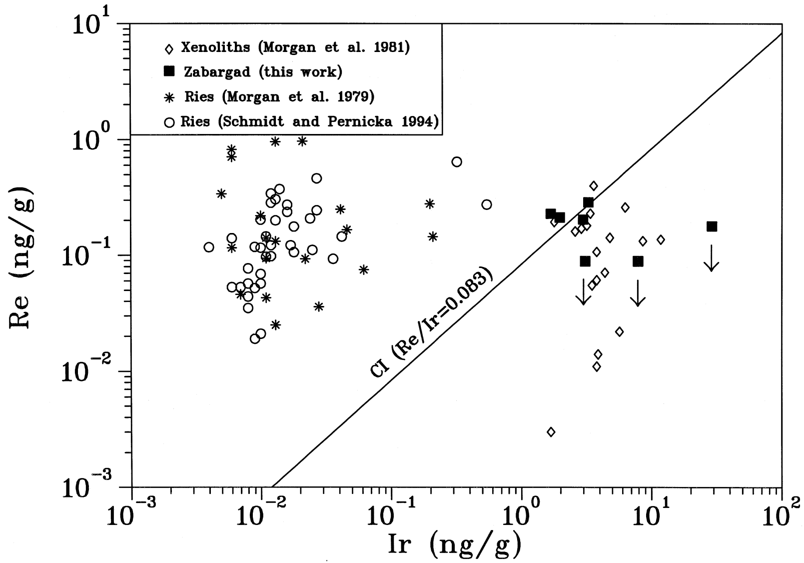

Fig. 5. Re vs. Ir in Zabargad samples and literature data for suevite samples and crystalline basement samples from the Ries crater. There is good agreement between the Re data for Ries samples from Schmidt and Pernicka (1994) obtained by NiS-extraction with data from Morgan et al. (1979) by radiochemical neutron activation analysis, supporting the reliability of the data obtained by NiS-extraction of Re.

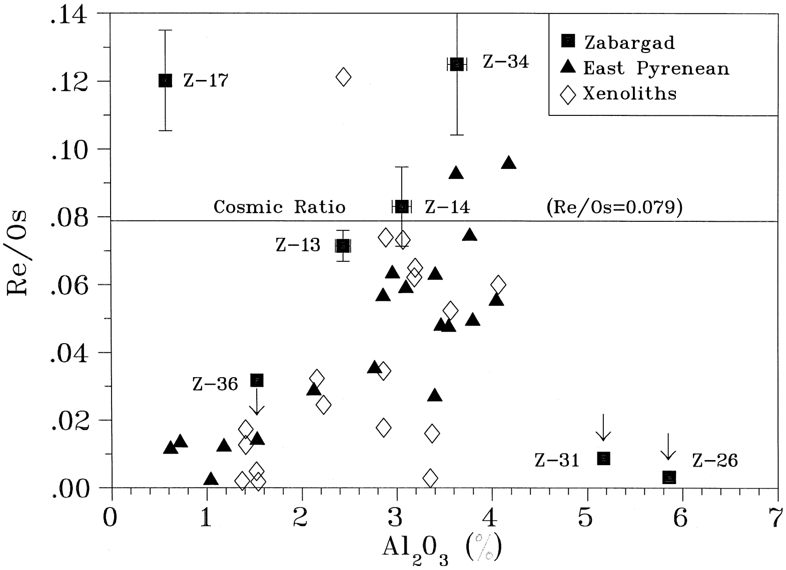

Fig. 6. Re/Os vs. Al_2O_3 for Zabargad rocks, for a suite of sample from the East Pyrenaen massive peridotites (Reisberg and Lorand, 1995) and for various xenoliths (Morgan et al., 1981). The approximate correlation of Re/Os with Al_2O_3 in the Pyrenaen samples and the xenolith data reflects simultaneous removal of Al and Re by partial melting. The high Re/Os-ratios in the Zabargad Z-17 harzburgite and in the spinel–plagioclase–lherzolite (Z-34) contradicts this trend. These samples were probably contaminated with a Re-rich phase.

ratio of 0.31. A higher than chondritic Rh/Ir ratio was also found in the Pyrenaen suite of ultramafics by Pattou et al. (1996). The average Rh/Ir ratio of 0.351 ± 0.044 obtained by these authors is between the ratio reported here and the CI-value. Also, the suite of oceanic peridotites reported by Snow and

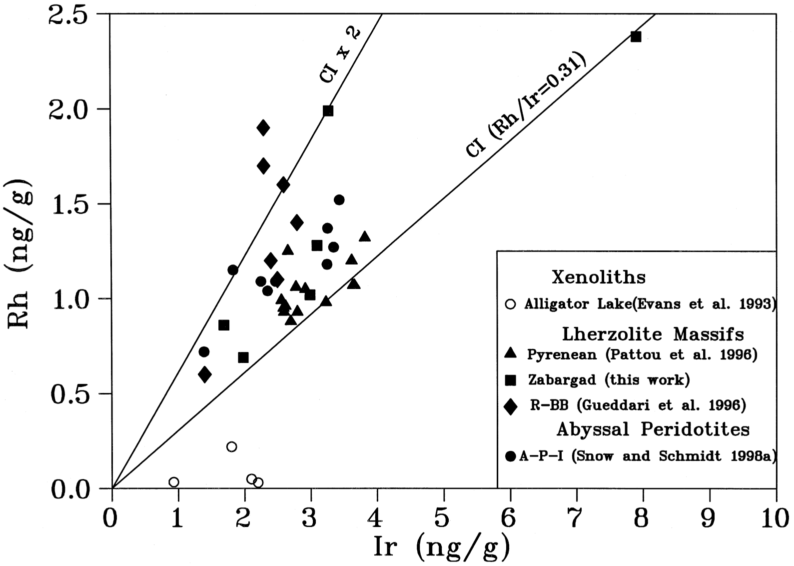

Fig. 7. Rh vs. Ir from Zabargad rocks (this work) and compared with literature data. The CI-chondrite ratio is indicated. There is an apparent enrichment of Rh in mantle rocks.

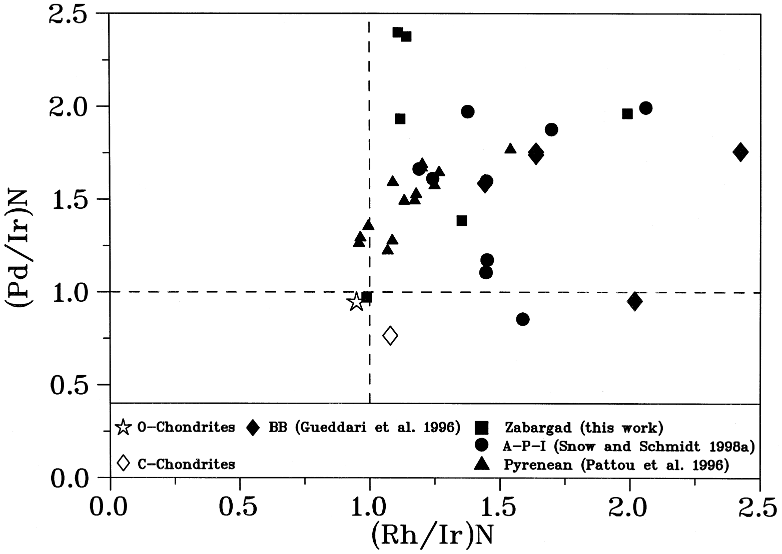

Fig. 8. CI-normalized Rh/Ir vs. Pd/Ir ratios of oceanic peridotites (Snow and Schmidt, 1998b), Pyrenaen peridotites (Pattou et al., 1996), peridotites from Ronda and Beni Bousera (Gueddari et al., 1996) and Zabargad rocks (this work). CI-normalized ratios for ordinary chondrites (OC) and carbonaceous chondrites (CC) from Wasson and Kallemeyn (1988), EC data from Hertogen et al. (1983).

Schmidt (1998a) show the same non-chondritic ratio as the Zabargad samples (Figs. 7 and 8).

Even stronger deviations from chondritic ratios are found for the Pd/Ir ratio (Fig. 9). The average ratio of the analyzed Zabargad rocks is 2.56 ± 0.53, more than a factor of two higher than the CI-chondritic ratio of 1.21. Again, the Pattou et al. (1996) data show a similar overabundance of Pd

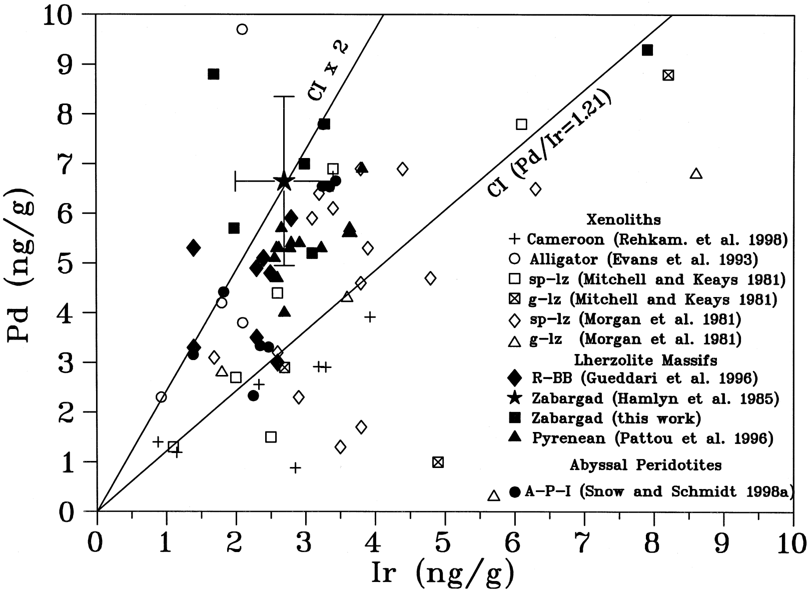

Fig. 9. Pd vs. Ir. The Zabargad samples (Z-26 is not shown), the Pyrenaen peridotites (Pattou et al., 1996) and the Ronda and Beni Bousera peridotites (Gueddari et al., 1996) have higher than chondritic Pd/Ir-ratios. Excess Pd is less obvious or even absent in the xenolith data by Morgan et al. (1981) and Mitchell and Keays (1981). See text for details. sp = spinel; g = garnet.

with a mean Pd/Ir ratio of 1.81 ± 0.06. However, Mitchell and Keays (1981) and Morgan et al. (1981) and Morgan (1986) observed, despite large variations, on average, chondritic Pd/Ir ratios in xenoliths from a variety of localities. The xenoliths from Cameroon Line, with their enhanced Ru/Ir ratios (1.74 ± 0.13) are not enriched in Pd, even slightly depleted, with an average Pd/Ir ratio of 1.09 ± 0.26 (Rehkämper et al., 1997). The oceanic peridotites are, on the other hand, characterized by an elevated Pd/Ir-ratio. A more detailed discussion of the behavior of Pd is given in a later section.

The comparatively low Au contents and the resulting high Ir/Au and Pd/Au ratios are typical of upper mantle rocks. The average Pd/Au ratio of the Zabargad samples is 10.32 ± 2.28 compared to the CI-ratio of 3.65. Morgan et al. (1981) found an average ratio of 9.41 ± 2.4 similar to the ratios determined by Mitchell and Keays (1981). Low Au may reflect low initial Au content in the material that provided the HSE for the Earth's mantle. The vapor pressure of Au is higher than that of Pd implying a lower condensation temperature and thus higher depletion in most meteorite groups. In addition it appears that variations in Au contents of upper mantle rocks exceed those of Ir and other more refractory metals (e.g., Spettel et al., 1991). Probably Au is more susceptible to alteration than the other PGE and it is therefore difficult to establish the primitive upper mantle Au-content.

8. Host phase of PGE in upper mantle rocks

The high PGE contents of the two Zabargad samples Z-26 and Z-31 demonstrate the presence of mobile components enriched in PGE. The pattern of PGE in the enriched sample Z-26 is very similar to that of most of the other samples, with a clearly resolvable Pd-anomaly. The only difference is some additional enrichment of Os in Z-26 compared to the other PGE which is not visible in any of the other samples, except for Z-31 (Fig. 1b). The otherwise similar pattern in the enriched and normal samples suggests a common host phase for both rocks. That this component is inhomogeneously distributed within the host rocks is seen from two additional analyses of Z-26. Although a similar high Ir content of Z-26 (28 ppb) as that found here (29.1 ppb) was reported earlier by Kurat et al. (1993) using instrumental neutron activation analysis, a sample of the same rock analyzed later gave only 3.2 ppb (B. Spettel, priv. communication). From the results of analyses of mineral separates Mitchell and Keays (1981) claimed that about 60% of the PGE in a spinel or garnet lherzolite is contained in sulfides while the rest is dissolved in solid solution in the major phases. Pattou et al. (1996) separated 15 mg of Fe–Ni–Cu sulfides from a Pyrenean spinel lherzolite sample. They found high enrichments of PGE in this sample, approximately 500 times the average content of PGE in upper mantle rocks, i.e., 0.2% of such a component would be sufficient to account for the bulk content of PGE in a given upper mantle rock. Magnetic separation of ''sulfides'' from two fertile spinel lherzolites by Jagoutz et al. (1979) produced a sample with Ir contents of 3.81 ppm and 5.58 ppm, respectively. This is in the same range as the 1.21 ppm found by Pattou et al. (1996) in their sulfide fraction.

One possible interpretation is that two components are present as PGE carrier phases, one hosted in sulfides and thus susceptible to mobilization and the other one immobile and locked up in host rock minerals as suggested by Mitchell and Keays (1981). The five Zabargad samples with ''normal'' upper mantle chemistry would then contain the immobile component while the two enriched samples had been affected by metasomatic processes providing the component with high PGE-contents. The source of the PGE is, however, for both components the same, the upper mantle. Either only a fraction of PGE is mobilized and extracted to form the mobile component or some parts of the mantle have lost their complete inventory of PGE in forming the mobile component. The first possiblity is more likely. Among the more than 50 peridotitic rocks of presumed upper mantle origin analyzed by INAA in the cosmochemistry department in Mainz (B. Spettel, priv. communication) is not a single sample with Ir below 1 ppb, i.e., none of the samples has lost PGE quantitatively by sulfide removal. The surprisingly uniform average HSE contents in upper mantle samples from different localities compiled in Table 4 also reflects the comparatively small variations of these elements in mantle rocks. To summarize this important point, the bulk of the PGE in upper mantle rocks do not appear to be concentrated in mobile sulfide phases. Although such phases are found, residues, i.e., samples devoid of PGE or with very low PGE contents are not, or rarely encountered, perhaps with the exception of the Tanzanian xenoliths analyzed by Rehkämper et al. (1997). Thus, if upper mantle PGE were concentrated in mobile phases much more variability in PGE contents in upper mantle rocks would be expected.

9. Origin of high Pd in Zabargad peridotites

One of the most obvious deviations from a chondritic PGE-pattern in the analyzed Zabargad rocks is the positive Pd-anomaly present in five of seven analyzed samples (Fig. 1b). It has been mentioned before that Pattou et al. (1996) found similar, although somewhat less pronounced, Pd-anomalies in Pyrenean lherzolites. Are abnormally high Pd contents confined to orogenic lherzolites? The Mitchell and Keays (1981) data tend to support such a contention. These authors found approximately chondritic Pd/Ir ratios in variety of xenoliths from localities in Australia, Africa and America. Coarse-grained garnet lherzolitic xenoliths from Matsoku have even subchondritic Pd/Ir ratios. The PGE data for the xenoliths of the UM series (Basaltic Volcanism Study Project, 1981; Morgan et al., 1981) appear to confirm these findings. Although there are comparatively large variation in Pd/Ir ratios, the average Pd/Ir is with 1.20 ± 0.13 essentially chondritic. The Rehkämper et al. (1998) data on fertile xenoliths from the Cameroon Line (Fig. 9) also do not indicate excess Pd. To the contrary, these rocks have Pd/Ir ratios slightly below CI (average 1.09 ± 0.26). The depleted Tanzanian xenoliths have even lower ratios (0.41 ± 0.38), excluding one anomalous sample. Eight of the nine oceanic peridotites analyzed by Snow and Schmidt (1998a) show, on the other hand, a clear excess of Pd reflected in the higher than chondritic Pd/Ir ratios (Fig. 9).

Thus, it can be concluded that there are considerable variations in Pd/Ir ratios in upper mantle rocks. The Pd-anomaly appears to be less pronounced in xenoliths from the sub-continental mantle, whereas massive peridotites and xenoliths from the oceanic mantle are characterized by high Pd/Ir ratios. However, as there is a large spread in Pd/Ir ratios in continental xenoliths, further analyses are required to better define the extent of the Pd anomaly. It is essential for understanding the origin of the excess Pd if the high Pd is a local or a global phenomenon. The presently available data suggest that the Pd anomalies reflect large inhomogeneities within the upper Earth mantle, on the order of hundreds of kilometers, as suggested by Pattou et al. (1996). It also appears, based on the limited data available, that excess Pd is not correlated with excess Ru as discussed above. Ruthenium excesses are probably global compared to the more local nature of the Pd excess.

There are a number of possible mechanisms to produce the Pd anomalies.

(1) A simple way to explain deviations from chondritic ratios is by assuming that the mantle PGE pattern is the result of core–mantle equilibrium at very high temperatures and pressures (Murthy, 1991). The mantle PGE pattern would then reflect the PGE metal/silicate partition coefficients at high p and T. Most of these partition coefficients would have to be nearly identical, only the Pd metal-silicate partition coefficient would have to be somewhat lower. However, as pointed out in the introduction core/mantle equilibrium for the HSE can be excluded. The experimentally determined metal/silicate partition coefficients of Pd, Ir, and Pt are very high, differ from each other, do not sufficiently decrease with temperature and Pd and Pt show no pressure dependence (Borisov et al., 1994; Borisov and Palme, 1995, 1997; Holzheid et al., 1997).

(2) Palladium and Au are, compared to Ir, Os and Ru, incompatible with major mantle minerals and they will therefore preferentially partition into the melt when large degrees of partial melting are considered, i.e., in the absence of a separate sulfide phase (e.g., Brügmann et al., 1987). Crystallization of such a high Pd melt would produce phases with high Pd/Ir ratios. Local addition of such components to the mantle (possibly as sulfide) would lead to excess Pd. The excess Au that should accompany excess Pd may remain unnoticed, as the bulk Earth probably has a Au/Pd ratio significantly below the CI-ratio, in accord with the general depletion of volatile elements in the Earth's mantle. The precise Au/Pd ratio of the upper mantle of the Earth is not known, because of mobilization of Au, leading to

large variations of Au in mantle rocks (e.g., Spettel et al., 1991). The excess Ru could not be explained by such a process, at least based on the data of Brügmann et al. (1987). However, partial melts should have high Re. But Re is depleted in the samples with high Pd enrichment.

(3) A popular hypothesis for the origin of PGE in the mantle is the addition of a late chondritic veneer (see Schmitt et al., 1983 and references therein) which would have delivered essentially unfractionated chondritic material to the Earth's mantle. With this type of model excess Pd is difficult to understand. The Pd-condensation temperature is in the range of condensation temperatures of Mg-silicates and metallic iron (Palme et al., 1988) and therefore, Pd is not fractionated relative to the major components (olivine, metal) in chondritic meteorites. However, refractory elements (e.g., Ca, Al, REE) are depleted in many groups of chondritic meteorites, most pronounced in enstatite chondrites. Enstatite chondrites have Al/Si ratios of 0.049 compared to 0.082 in CI-chondrites (Wasson and Kallemeyn, 1988). The depletion of the refractory metal Ir should be reflected in nearly twice the CI-ratio of Pd/Ir. The average Pd/Ir ratio of 6 enstatite chondrites analyzed by Hertogen et al. (1983) is with 1.33 only slightly above the CI-ratio of 1.21. Apparently, refractory element depletion in enstatite chondrites is less pronounced for siderophile elements than for lithophile elements. It is thus concluded that the range in Pd/Ir-ratios of chondritic meteorites is too small to produce the observed upper mantle variations in Pd/Ir ratios (see Fig. 8). There is, of course, the possibility that the late veneer had Pd/Ir ratios much higher than those in the various meteorite groups. This cannot be excluded, but is, in view of the otherwise chondritic signature of the late veneer, unlikely.

(4) In the late veneer hypothesis it is generally assumed that the mantle was free of PGE before the late bombardment established the present level of HSEs in the Earth's mantle. The comparatively high abundances of PGE, Au and Re that must have accompanied Ni, Co, etc., in an earlier stage of accretion are assumed to have been extracted into the core prior to the addition of the late veneer, either as sulfides or with Ni-rich metal (Schmitt et al., 1983; O'Neill, 1991). Recent determinations of solubilities of PGE in silicate melts have shown that PGE metal/silicate partition coefficients are very high and variable for the various PGE (Borisov et al., 1994; Borisov and Palme, 1997). The Pd-metal/silicate partition coefficient, for example, is at 1350°C around 10^7, those for Ir and Pt are several orders of magnitude larger. Only about 10^{-2}% of a metal component is required to reduce the Pd content from a chondritic level to that observed in the upper mantle. As Ir and Pt have much higher metal/silicate partition coefficients these two elements would have been extracted much more efficiently into the core and the residual mantle would have retained some Pd leading to a pre late veneer Pd-anomaly. Extraction of PGE from the mantle would not affect the abundances of other, less siderophile elements, such as Fe, Ni, Co, Ga, as these elements have much lower metal/silicate partition coefficients. This and the previous hypothesis may be difficult to reconcile with the rather local character of the Pd anomaly.

(5) Another possibility is the presence of residual metal phases in the Earth's mantle that escaped core formation and were later oxidized (Jones and Drake, 1986). This model for establishing the abundances of siderophiles in the mantle involves oxidation of residual core metal. Jones and Drake (1986) did not include Pd in their suite of elements. However, the Ir metal/silicate partition coefficients they have used in their model are much lower than recent experimental results indicate (Borisov and Palme, 1995). It is thus doubtful if this type of model can successfully predict upper mantle siderophiles, in particular abundances of HSE.

(6) Recently, McDonough (1995) suggested that the HSEs in the mantle were delivered by a small fraction of metal that separated from the outer core after core formation. In this model excess of Pd would not be unreasonable. If equilibrium between outer and inner core is assumed and adopting models of asteroidal core formation inferred from iron meteorites (Walker et al., 1995) refractory metals such Ir, Os, etc., should be concentrated in the solid inner core, judging from experimentally determined liquid–metal/solid–metal partition coefficients (e.g., Scott, 1979). Snow and Schmidt (1998a) have attempted to include the excesses of Ru and Rh in such a model by postulating inner core–outer core fractionation of these elements. In this kind of mod-

els, local variations in the Pd excess within the mantle would reflect inhomogeneous distribution of the core component. It is, however, by no means clear if liquid metal/solid metal partition coefficients controlling the distribution of Ir, Pd, etc., in a cooling asteroidal metal melt at low pressures, have any significance for inner core/outer core fractionation at millibar pressures and several thousand degree centigrade.

(7) Another possibility is the addition of a crustal PGE component to mantle rocks. The PGE, Pd, Ru, Rh and Pt are enriched in the crust relative to Ir and Os (Schmidt et al., 1997; Schmidt and Palme, 1998). Addition of a few percent of a crustal component would, however, not provide enough Pd, etc., to produce the observed excess, as the crustal content of Pd is about one third of that of the mantle. Addition of a sulfide phase that had pre-concentrated crustal PGE would be required to produce the observed pattern. However, the crust also has comparatively high Pt contents, with a crust mantle ratio of about 1/6 compared to 1/100 for Ir (Schmidt and Palme, 1998). Addition of a crustal component would therefore also provide excess Pt. However, the Pyrenaen data of Pattou et al. (1996) show perfectly chondritic Pt/Ir ratios despite significant enhancement in Pd, i.e., high Pd/Ir ratios.

In a recent paper Rehkämper et al. (1997) showed that depleted xenoliths from northern Tanzania have much more fractionated patterns of PGE than the more fertile xenoliths from the Cameroon Line. The fractionated PGE patterns in the Tanzanian rocks are explained by the authors as resulting from ‘‘fluid-phase transport processes and multiple episodes of melt depletion’’. Most of these PGE patterns are much more fractionated than the PGE patterns discussed in this paper. The observed Pd excess, discussed here is a characteristic feature of otherwise chondritic patterns, unlike most of the Tanzanian xenoliths patterns with large deviations from chondritic ratios. These rocks may indeed have been processed much more extensively than the rocks discussed here.

It thus appears that there is no simple explanation for the Pd excess and related excesses of Ru and Rh. Before a better judgment on the origin of the Pd anomaly can be made, it is important to understand the spatial extent of the high Pd, is it confined to massif peridotite bodies of shallow upper mantle origin? Is there a correlation in xenoliths of Pd excess with depth? Or is the Pd excess a mantle-wide signature with only few exceptions? In addition, more and better data on Os, Ru, Rh and Pt are required to better define the deviations of Ru/Ir, Rh/Ir and possibly Pt/Ir ratios from chondritic ratios. Correlations among these anomalies may provide strong constraints on their origin and thus provide important new insights into accretion of the Earth and evolution of the Earth’s mantle.

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Appendix A. Sample description

Z-13 Sp-lherzolite. Main Peridotite Hill (MPH). Elevation 165 m. Fresh, coarse-grained, porphyroclastic texture with slightly deformed orthopyroxene porphyroclasts. Very thin exsolution lamellae of clinopyroxene in orthopyroxene, large clinopyroxene grains have orthopyroxene exsolution lamellae. Spinel is brown and mostly associated with olivine. The latter shows kink bands. The matrix is recrystallized and contains neoblasts of olivine and orthopyroxene.

Z-14 Sp-plag-lherzolite. MPH. Elevation 170 m. Fresh, coarse-grained lherzolite with abundant large, macroscopically black spinel neoblasts on shear planes. Texture is porphyroclastic and foliated. The large (up to 1 cm) spinel neoblasts are emplaced in the follation plane; they are green in transmitted light; matrix spinel is brownish-green. All spinels (green and brownish) are surrounded by plagioclase; coronas of orthopyroxene and clinopyroxene are present at contacts between olivine and plagioclase.

Z-34 Sp-plag-lherzolite. Main rock type of Central Peridotite Hill (CPH). Coarse-grained, porphyroclastic with some grain boundary recrystallization; large orthopyroxene has very thin exsolution lamellae of clinopyroxene and inclusions of olivine; clinopyroxene has broad orthopyroxene exsolution lamellae; brown amphibole occurs interstitially; olivine porphyroclasts have kink bands and occasionally include spongy orthopyroxene and small rounded spinel; larger holly-leaf spinel (green) is surrounded by plagioclase.

Z-17 Amph-harzburgite. The sample is taken from a talus on shore just below the peridotite mass of the Northern Peridotite Hill (NPH). Macroscopically the sample is fine-grained and sheared. The texture is equigranular with rare porphyroclasts and shows evidence of complex tectonic history (repeated decrease in grain size and recrystallization), brown spinel is situated mostly in the foliation plane; abundant neoblasts of amphibolite.

Z-26 Plag-wehrlite. From MPH near SW tip of the island. Macroscopically foliated with abundant black (green in thin section) spinel (up to 2 cm); in thin layers parallel to foliation; spinel rimmed by plagioclase; macroscopically the rock is strongly deformed with a complex porphyroclastic texture; abundant olivine (kink banded) and clinopyroxene porphyroblasts; orthopyroxene porphyroclasts show exsolution lamellae; coarse-grained, twinned plagioclase is abundant and tends to occur in strings parallel to foliation

Z-31 Orthopyroxenite. From a vein on CPH. Very coarse-grained, pegmatoidal rock with orthopyroxene up to 10 cm; orthopyroxene has clinopyroxene exsolution lamellae in the interior but not near surface; a few clinopyroxene with exsolution lamellae of orthopyroxene are included in orthopyroxene; olivine and spinel (brown) are present only in minor amounts.

Z-36 Amph-dunite. Collected on shore of NPH. Deformed rock with abundant large porphroblasts of green amphibolite; texture is transitional between porphyroclastic and equigranular with good orientation of neoblasts along foliation; minor amounts of orthopyroxene and apatite are present in the matrix.

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