

Full Length Research Paper

Isotope dilution with high pressure asher acid digestion for the determination of platinum group elements in chromitite from katpal chromite mine in the Sukinda Ultramafic Complex, Eastern India

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Chromitite samples were collected from a core from the Katpal chromite mine of Sukinda chromite field for characterization of mineralogy especially the platinum group minerals (PGM). Isotope dilution with High Pressure Asher (HPA-ID) technique has been used in this study to evaluate its ability to determine compositions from small quantities of sample (two grams of sample). Enrichment of Iridium group of platinum elements (IPGE) (Ir ~ 1717 ng/g; Ru ~ 20 ng/g) at depth of ~ 35-80 m in the investigated core suggests the presence of a strong potential zone for IPGE mineralization. The obtained data suggests similarities with the 'Reef-type' mineralization.

Key words: Platinum group minerals (PGM), high pressure asher acid digestion (HPA-ID), iridium group of platinum elements.

INTRODUCTION

The Sukinda ultramafic complex hosts the single largest opencast chromite mining area in Orissa, India (Banerjee, 1972; Chakraborty and Chakraborty, 1984; Page et al., 1985; Varma, 1986; Pal and Mitra, 2004). It is pertinent to note that the chromite resources of Orissa account for ~98% of the total resources of India (Mondal et al., 2006) and are fourth in terms of identified global resources (Vermaak, 1987). In 2009, India contributed 17% chromite (global total production 23, 000,000 tonnes) and stand second in the global rankings (SEG News Letter, 2010). The Katpal Ultramafic Body (KUB) is part of the Sukinda ultramafic complex and is the least studied part of the complex in terms of the Cr,Ni-Cu-PGE

mineralisation (Sarkar et al., 2003; Sen et al., 2005). It has been observed that rocks of Sukinda area are highly lateritised (Basu et al., 1997) with complete alteration of the primary mineralogy up to ~ 30 m depth. The studies on chromite occurrences in India are very few and detailed investigations in terms of tectonic setting and evaluation of their potential as future targets for platinum exploration is highly significant and relevant (Mondal et al., 2006).

Chromite-bearing samples are resistant to traditional acid digestion or by using more modern methodologies such as aqua regia digestion, Microwave digestion or Li tetra borate route (Merkle et al., 2008). Therefore, here we report an attempt using isotope dilution coupled with high pressure acid digestion followed by ICPMS, for the determination of platinum group elements of chromite-bearing samples from KUB. An attempt was also made to understand the IPGE mineralisation in the KUB in terms

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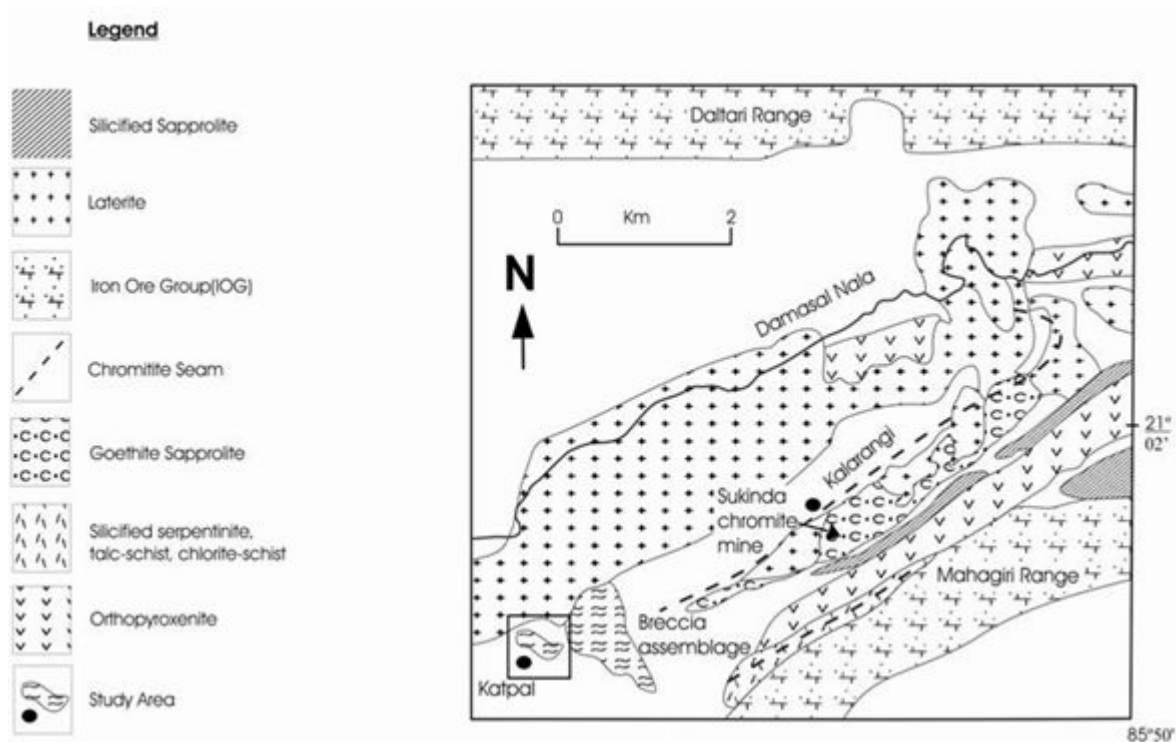


Figure 1. Geological map of Sukinda Massif (after Page et al., 1985).

of evaluating its potential for PGM mineralization.

Geology of the area

The Sukinda ultramafic complex forms part of the Singhbhum craton of the Indian peninsula. Dismembered chromite-bearing ultramafic bodies occur sporadically in an area of 420 sq. km around Sukinda within latitudes 20°53' and 21°05' and longitudes 85°40' and 85°53' (Banerjee, 1972; Page et al., 1985). The ultramafic rocks are composed of orthopyroxenites, dunites, and chromitite. The Katpal ultramafic body (KUB) lies ~12 km towards SW in the same strike direction as Sukinda ultramafic field at latitude 21°01'N and longitude 85°43'E (Figure 1). Similar to the brecciated chromites of Nuasahi massifs (Mondal and Baidya, 1997), from which PGE mineralisation is reported (Auge and Lerouge, 2004), brecciated chromitite bodies are also reported at Katpal area (Sarkar et al., 2001). The regional stratigraphic sequence at Katpal from the bottom upwards, is orthopyroxenites, silicified serpentinite, talc schist, chlorite schist, iron ore group, chromitite seams, with laterite and soil cover (Mondal et al., 2001). In the Sukinda ultramafic complex, various types of chromite ore viz. massive, spotted, laminated, and friable have been recognized (Chakraborty et al., 1984) and these types are different from the chromites (viz. lumpy, brecciated and in layered form) of KUB.

Borehole description

For the present study, samples representing different mineralized horizons of the drill core-201 (up to a depth of ~120 m) were selected. The borehole stratigraphy (Figure 2) shows soil cover (lateritised) to a depth of ~0 - 1.2 m, which is followed by weathered serpentine to a depth of ~28 m. The altered serpentinite contain brecciated chromite grains in varying sizes (0.5 - 2 cm). Serpentinised ultrabasic is recorded from 27.90 - 74.80 m. At 84 to 95 m, a chromitite layer (0.1 - 2 cm) cut the chromitite horizon up to 102 m. Based on the least alteration characters of chromite, the chromitites from 25.10 - 27.90 m (Figure 3) and 74.80 to 97.60 m (Figure 4) is utilized for the present investigation.

METHODOLOGY

The isotope dilution is one of the most precise and sensitive analytical techniques for determination of platinum group element concentrations in chromitites (Potts, 1987; Paliulionyte et al., 2006). A high pressure asher (HPA-S, Anton Paar®) with 7x50 ml quartz vessels was used for acid digestion of the samples. A Perkin Elmer SCIEX 6000 in Memorial University, Canada is utilized for this work. The standard configuration with a concentric nebulizer in a Scott type double pass spray chamber was used for analysis. The ion lens voltages were optimized with a 5 ng/ml tuning solution. The lens voltages were varied to obtain a high sensitivity for ¹¹⁵In (Indium). The instrumental parameters are outlined in Table 1. The sample dissolutions were carried with hydrochloric acid (30% m/m)

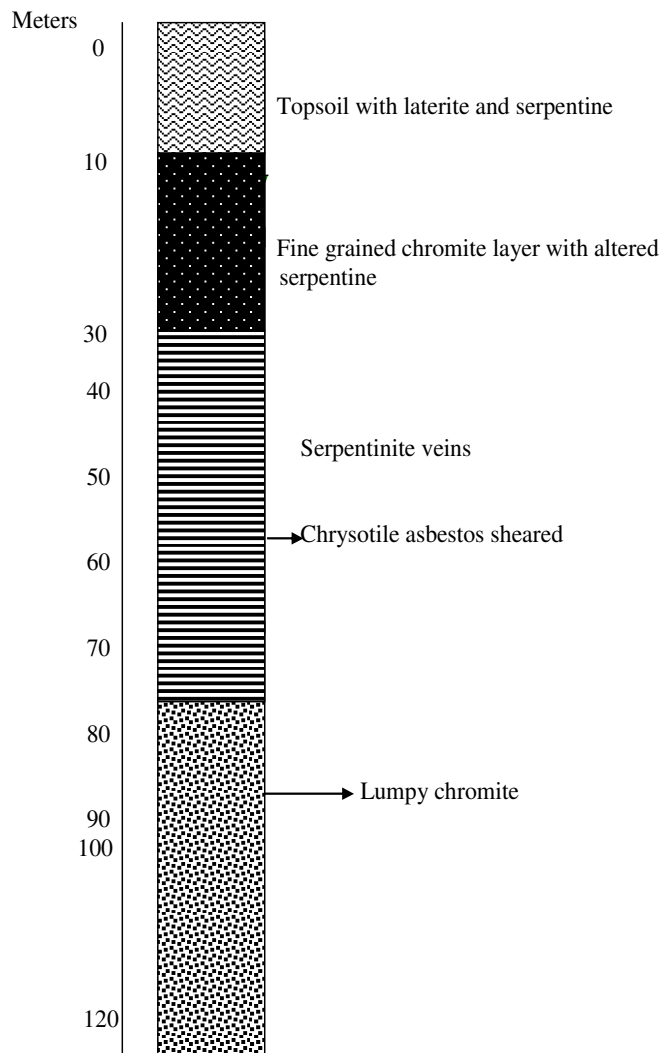


Figure 2. Columnar section of the drill core from borehole 201, Katpal ultramafic body (KUB), Sukinda Ultramafic Complex,

and 65% m/m nitric acid (trace grade, Fisher®).

A cation exchange resin Biorad®AG50Wx8 (200-400 mesh) (Biorad Lab, USA) in H⁺ (ion) form was used for off-line chromatographic separation. Calibration solutions were diluted from 10 µg/ml precious metal (Ru, Pd, Rh, Re, Os, Ir, Pt, Au) multi element solutions traceable to NIST (Inorganic Ventures, USA). The foremost step in Isotope dilution technique is to obtain a calibrated spike. In this context a spike was developed at Memorial University, Canada. Two grams of finely powdered homogenized sample were spiked with enriched ⁹⁹Ru, ¹⁰⁵Pd, ¹⁹¹Ir and ¹⁹⁴Pt, and digested in a HNO₃/HCl (5:2) acid mixture at 300°C for 15 h. The pressure was adjusted to 100 bars at the beginning and increased to 125 bars during digestion. After removing undissolved solids by centrifugation and concentrated acids through gentle heating on a hot plate, the solution was dissolved in 5 ml 0.1 M HCl and loaded after filtering onto a cation exchange column, filled with Biorad® AG50Wx8 resin. 0.1 M HCl acted as the mobile phase during matrix-analyte separation. In dilute acid, matrix cations such as Fe³⁺ remained on the column whereas the eluent transported the anionic PGE chloro-complexes through the resin. The solution thus obtained was analyzed by ICP-MS with hydrogen as (Collision

Reaction Interface) CRI gas (Table 2). The standard reference material (WMS-1 and SU-1b) was prepared following the above procedure along with the samples and were used for calibrating and checking accuracy/precision of the analysis.

The SX-100 Cameca electron microprobe (EPMA) at National Geophysical Research Institute (NGRI), was utilised to carryout analysis of selected mineral grains. Pictures of Platinum Group Minerals (PGM) were taken in backscattered mode and possible PGM phases were classified using manual elemental identification Wavelength dispersive spectrometer scans (WDS scans), with spectral acquisition time of 100s with a 20kV and 20 nA beam.

RESULTS AND DISCUSSION

During the course of this study, three distinct platinum-group mineral phases were observed. Platinum-group minerals were identified based on WDS and microprobe analysis. All the platinum group elements were at sulphide-sulphide grain boundaries, or at grain boundaries of basemetal sulphide with silicate and chromite. The phases were classified according to the presence of elemental characteristics. Due to resolution and limitations during analysis of small platinum-group mineral grains included in basemetal sulphide and interferences of nickel, copper, cobalt and iron could not always be established. The following three phases are prominent: Ru-S (laurite) (Figure 5), Os-Ir-Ru-S (composite of Os-Ir alloy and laurite), As-Os-Ir-Ru (Omeiite). The results obtained from HPA-ID (Table 3) show high concentrations of Pt and Ir (~ 280 ng/g and Ir ~1717 ng/g). A scatter plot showing interrelationships amongst Pt, Pd, Ir and Ru is shown in Figure 6. In a binary plot of Ir vs Ru (Figure 7), it shows positive linear trend and suggest that Ir and Ru is strongly controlled by laurite grains and Pt may be occurring as discrete phases or as alloys in basemetal sulphides. The osmium results obtained are generally not reported because of its volatile nature (Richardson and Burnham, 2002). However Os has been reported by (Meisel et al., 1996).

The correlation coefficients in Table 4 show a strong correlation between Ru and Ir and as expected we have a weak correlation between Pd and Ir. This signifies that laurite occur in solid solution rather than discrete phases in chromite grains. A number of studies on sulphide-poor Ultramafic- mafic volcanic rocks and plutonic rocks have shown positive correlations between Os, Ir, and Ru (IPGE) vs. Cr suggesting a genetic link between these enrichments (Naldrett and Gruenewaldt 1989; Scoon and Teigler, 1994; Stockman and Hlava, 1984; Teigler, 1999). These correlations indicate that IPGE could be controlled by chromite and that IPGE partition in to it. The partitioning of IPGE in chromite have been proven experimentally under oxidizing conditions (Fayalite-Magnetite-Quartz buffer) and these elements can partition into spinel (Capobianco and Drake, 1990; Capobianco et al., 1994; Richter et al., 2004; Homolva et al., 2008). However studies have shown that laurite (Ru[±Os±Ir]S₂) and Os-Ir rich alloys are most often



Figure 3. Core box showing chromitite at depth of 27.90 m.



Figure 4. Core box showing chromitite at depth of 79.80 m.

present as small discrete grains included in plutonic chromite (Prichard et al., 1981; Stockman and Hlava, 1984) they have been observed in environments of volcanic chromite also (Fiorentini et al., 2004; Locmelis et al., 2009). This may suggest, that chromite could be a carrier of these elements. In global scenario MSS (monosulfide solid solution) in natural sulfur rich magmatic systems would be expected to be enriched in

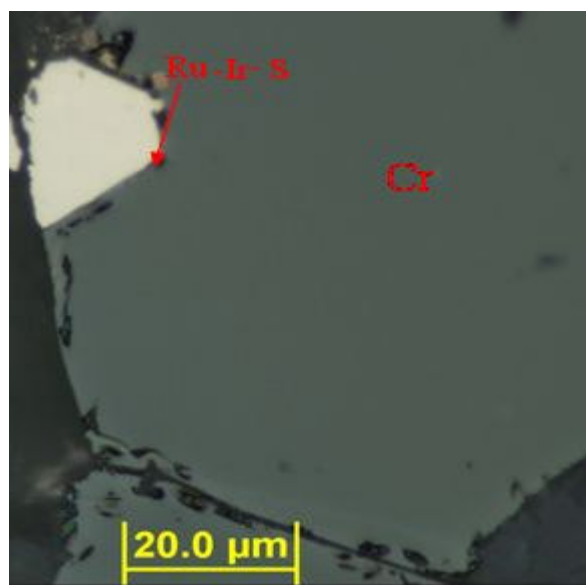
the IPGEs (Ir, Os and Ru) and Rh. These elements would then be present in solid solution within the cooling products of mss: Pyrrhotite and pentlandite rather than discrete phases. Capobianco et al. (1994) showed that Ru and Rh partition into oxides, but Pd does not. They suggested that oxide provokes the crystallization of the Os, Ir and Pt clusters whereas Ru and Rh are incorporated into the oxide structure. Adopting this, one

Table 1. Instrumental operating parameters.

Parameter	Value
RF Power	1100 W
Plasma gas	18 L/min
Auxillary gas	1.20 L/min
Nebulizer gas	0.79 L/min
CRI (H ₂ gas)	90 ml/min
Readings	1
Replicates	3
Scan mode	Peak hopping
Dwell time per AMU	10 ms

Table 2. Isotopic abundances of the spike.

Spiked isotope	Abundance (%)	Reference isotope	Abundance (%)
⁹⁹ Ru	98.63	¹⁰¹ Ru	0.49
¹⁰⁵ Pd	97.27	¹⁰⁶ Pd	1.85
¹⁹¹ Ir	98.17	¹⁹³ Ir	2.72
¹⁹⁴ Pt	97.00	¹⁹⁵ Pt	2.06

**Figure 5.** Photomicrograph showing laurite (Ru [±Os±Ir] S₂) grain in chromite.

could suggest that when chromite segregated from the hybrid magma Ru, and to a lesser extent Rh, partitioned into the chromite and that destabilized the cluster, resulting in the co-precipitation of chromite and the clusters to form chromite-rich layers enriched in all the PGE except for Pd. This could be a possible reason for

Table 3. HPA-ID results for PGE.

Code	Mode	Ru	Pd	Ir	Pt
S001098	H2	11	9	475	93
	Norm	17	3	449	93
S001099	H2	18	10	350	61
	Norm	24	3	316	58
S001100	H2	13	6	253	279
	Norm	26	1	308	265
S001101	H2	20	3	1747	39
	Norm	20	0	1717	32
S001102	H2	18	8	898	55
	Norm	29	1	908	52
S001103	H2	19	8	1089	44
	Norm	41	0	996	37
S001104	H2	22	8	998	94
	Norm	35	0	999	87

All values are in ng/g.

Table 3b. HPA-ID statistical presentation.

	Statistics			
	Pt	Ru	Ir	Pd
N	7	7	7	7
Mean	95.00	17.29	830.00	7.43
Median	61.00	18.00	898.00	8.00
Range	240	11	1494	7
Minimum	39	11	253	3
Maximum	279	22	1747	10

All values are in ng/g.

low Pd contents in our samples. Studies on the layered intrusions suggest that laurite is the most common inclusion in chromite of chromitite layers in the Stillwater Intrusion Complex (Talkington and Lipin, 1986), the Bird River Sill (Ohnenstetter et al., 1986) and the Bushveld Complex (Merkle, 1992). Taking in to consideration the available global data on Ir, Ru, Pt and Pd from chromitites of Merensky Reef, UG-2, LG, (South Africa) Konder (Brazil), Tulemann chromitite (Canada) and primitive mantle, our data is in comparison with reef type occurrence such as Merensky (data taken from Grunewaldt and Merkle, 1995) (Figure 8). Laurite is the most abundant Ir bearing mineral enclosed within chromite

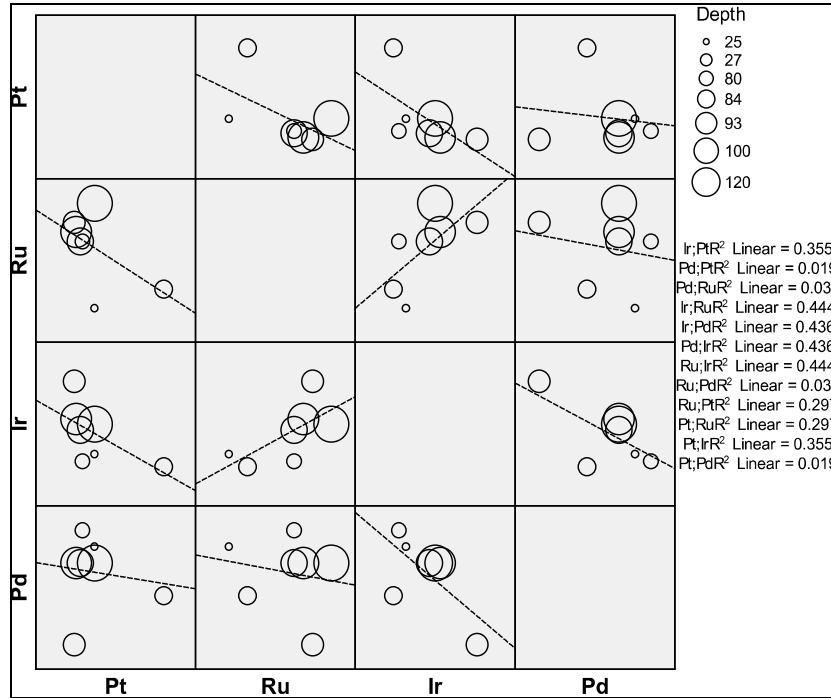


Figure 6. Scatter diagram showing interrelationships amongst Pt, Ru, Ir and Pd.

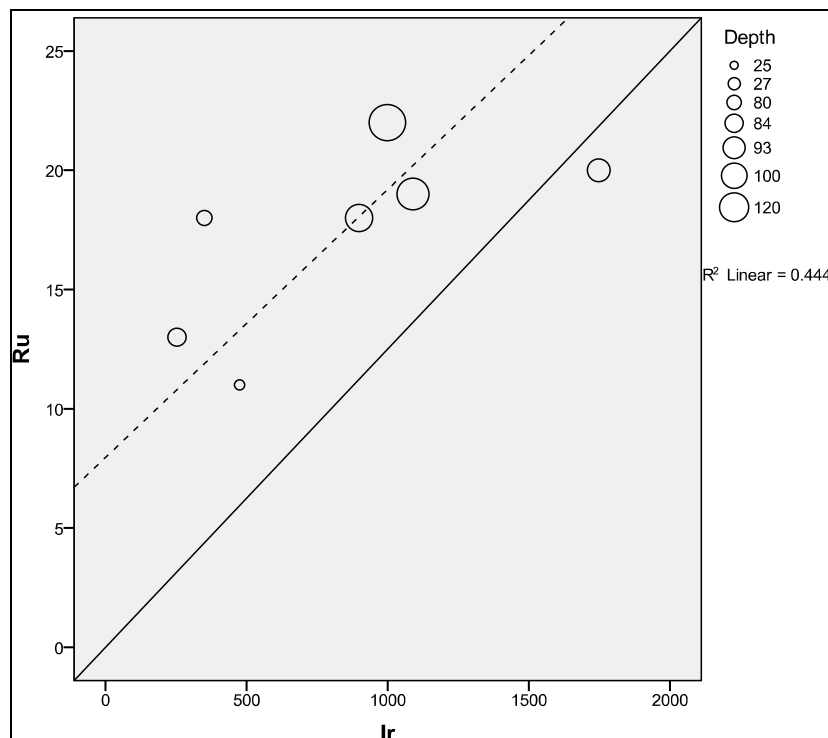


Figure 7. Binary diagram showing Ir vs Ru.

chromite in the Bushveld complex (Merkle, 1992). The high Ir content in our samples was corroborated with the presence of laurite grains in chromite.

Conclusions

High pressure asher-isotope dilution (HPA-ID) can be an

Table 4. Correlation coefficient

		Correlations				
			Pt	Ru	Ir	Pd
Spearman's rho	Pt	Correlation coefficient	1.000	-0.378	-0.750	0.185
		Sig. (2-tailed)	0.0	0.403	0.052	0.691
		N	7	7	7	7
	Ru	Correlation coefficient	-0.378	1.000	0.757*	-0.355
		Sig. (2-tailed)	0.403	0.0	0.049	0.434
		N	7	7	7	7
	Ir	Correlation coefficient	-0.750	0.757*	1.000	-0.408
		Sig. (2-tailed)	0.052	0.049	0.	0.364
		N	7	7	7	7
	Pd	Correlation coefficient	0.185	-0.355	-0.408	1.000
		Sig. (2-tailed)	0.691	0.434	.364	0.0
		N	7	7	7	7

*.Correlation is significant at the 0.05 level (2-tailed).

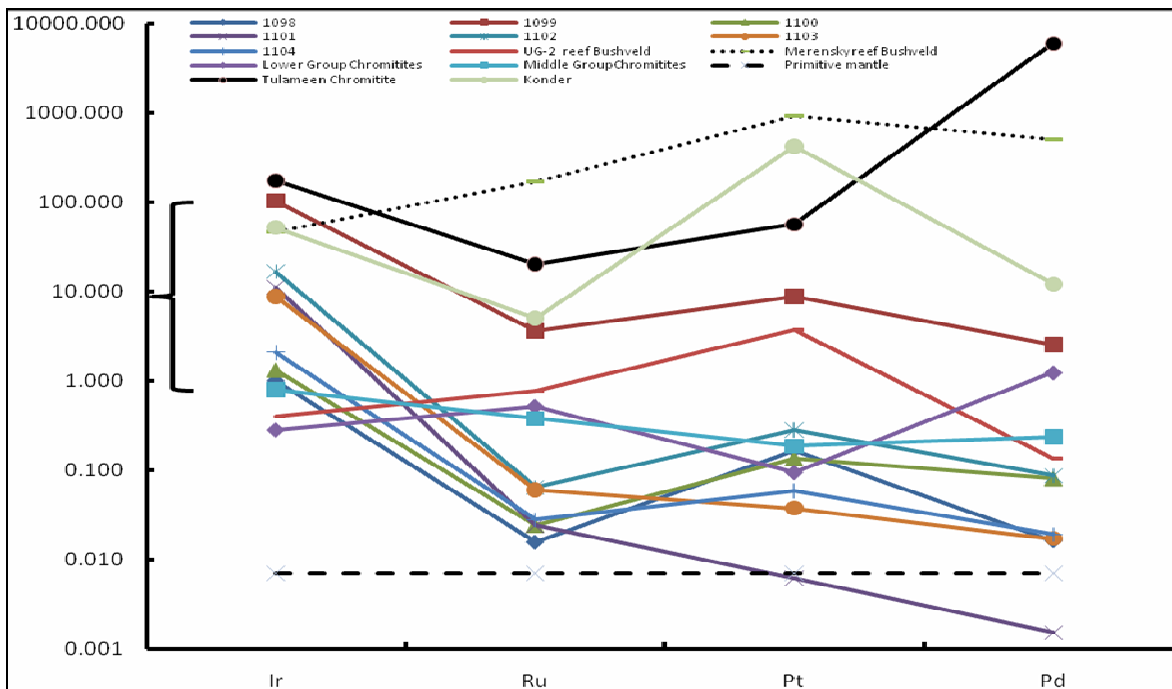


Figure 8. Comparison of Ir, Ru, Pt and Pd with global occurrences.

alternate technique to determine low concentration levels of platinum group elements. The technique utilizes only two milligrams of sample. Our studies prove the enrichment of high Iridium content up to 80 m depth in a core at Katpal ultramafic body of the Eastern India and this is well corroborated with the presence of Ru-Ir

bearing minerals. It could be possible, that stringers of chromitite bands contain the PGMs. Enrichment patterns of IPGEs in the samples show similarities with Merensky reef in Bushveld Complex, South Africa. It may be premature to draw authentic conclusion with Merensky reef type, until further detailed investigations are carried

out. However, considering the cost of exploitation, Katpal may need detailed multidisciplinary studies (including geophysical) with more bore hole drilling for systematic sampling. This study show unusual type of precious metal mineralisation in metamorphosed ultramafic terrains and areas hosting similar geology may need detailed studies.

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