Gold, silver and platinum group of elements mineralization in Precambrian uraniferous quartz-pebble conglomerates of Mankarhachua area, Angul District, Odisha

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The occurrence of gold, silver and platinum group of elements is reported from the Precambrian uraniferous quartz-pebble conglomerate (QPC) horizons at Mankarhachua area in the Precambrian Mankarhachua basin situated at the southwestern part of the Singhbhum–Orissa craton. Scanning electron micrographs show native gold grains and unidentified platy silver-bearing minerals. Chemical analysis of the host QPC samples shows significant abundances of gold and silver and anomalous content of platinum group elements. Platinum, ruthenium and rhodium dominate over palladium. This communication focuses on the gold and silver abundances, their distribution, host-rock characteristics and preliminary study on the control of mineralization.

Keywords: Gold, quartz-pebble conglomerate, platinum, silver.

THE importance of gold and silver cannot be overemphasized. In the modern world, they play a major role in international finance, medical and various modern industrial applications, besides their widespread use in jewellery. Between 2000 and 2010, the price of both the metals soared more than 200% throughout the world, primarily due to weakening of the US dollar. In India, therefore, exploration and production of gold and other precious metals is being given more emphasis to reduce the gap between supply and the growing national demand.

Gold occurs in variety of geological settings. In India, the most productive gold mines are associated with linear schist belts (greenstone belts) of Kolar, Hutti and Ramagiri in the eastern Dharwar craton of Neoarchean age[1]. However, in the global scenario, this type of deposit is second compared to sediment-hosted deposits in quartz-pebble conglomerates (QPCs). More than half of the present world's annual gold production is supplied from such QPC-type deposits like Au–U-bearing QPC-type deposit of Witwatersrand, South Africa, whose ore contains 1–25 g/t gold together with an average of 0.025% U_3O_8. Worldwide, similar Precambrian QPC occurrences are known in many Archean cratons, as part of siliciclastic placer deposits resting unconformably over Archean granite–greenstone terrains and formed under fluvio-deltaic environment in a largely anoxic atmosphere[2–4]. Such QPC occurrences contain allogenic grains of pyrite together with gold, silver, platinum group minerals (PGMs), uraninite and other detrital radioactive minerals. They often, singly or collectively, constitute a significant source of large tonnage, multi-metallic gold ± silver ± PGM ± U-bearing deposits with or without diamond and have significant economic potential[5].

In India, Precambrian Dharwar craton and Singhbhum craton are known to contain traces of gold in QPC-hosted radioactive anomalies. Walkunji uraniferous QPC of the Bababudan Group at the base of the Dharwar Supergroup in the Western Ghats has up to 0.2 g/t gold. Arbail occurrence belonging to the Chitradurga Group contains up to 1.5 g/t gold[6]. In Singhbhum craton, a few radioactive QPC occurrences in the Iron Ore Group (IOG) basins surrounding the Singhbhum Granite batholith, and the basal sediments of the Dhanjori volcano-sedimentary basin, show presence of gold. The localities from which gold in QPC is reported are as follows: up to 1.88 g/t gold at Ramchandrapur QPC in Malayagiri–Bankhol IOG basin, 0.2–0.7 g/t in Dhosra Parbat, 0.4–0.8 g/t in Turliga Parbat radioactive QPCs in the Garumahishani–Badampahar IOG basin[7,8], up to 0.3 g/t gold in Soyamba–Taldih radioactive QPC of Koira IOG basin[9]. Gold (0.33–1.28 g/t and up to 7 g/t in one sample) and silver (15–215 g/t)-bearing uraniferous QPC occurrences have also been reported from siliciclastic sediments in the lower part of the Dhanjori Group near Haludbani sector[10].

In this communication, we report the discovery of significant concentrations of gold and silver and anomalous values of PGE in radioactive QPC occurrence near Mankarhachua village, north of Pallahara town, Angul district, Odisha, in the Precambrian Mankarhachua basin, situated at the southwestern corner of the Singhbhum craton (in parts of Survey of India topographic sheet no. 73G/3).

Recent exploration by Atomic Minerals Directorate (AMD) in the Precambrian siliciclastic succession of Mankarhachua basin, situated in the southwestern corner of Singbhum craton led to the discovery of occurrence of uranium-bearing radioactive QPC horizons[11]. Mankarhachua siliciclastic succession occurs as detached outliers over the mafic metavolcanics to the north. In the south, they are in tectonic contact with Pallahara granite gneiss, marked by E–W trending 12 km long Mankarhachua Fault running near the southern boundary of the basin

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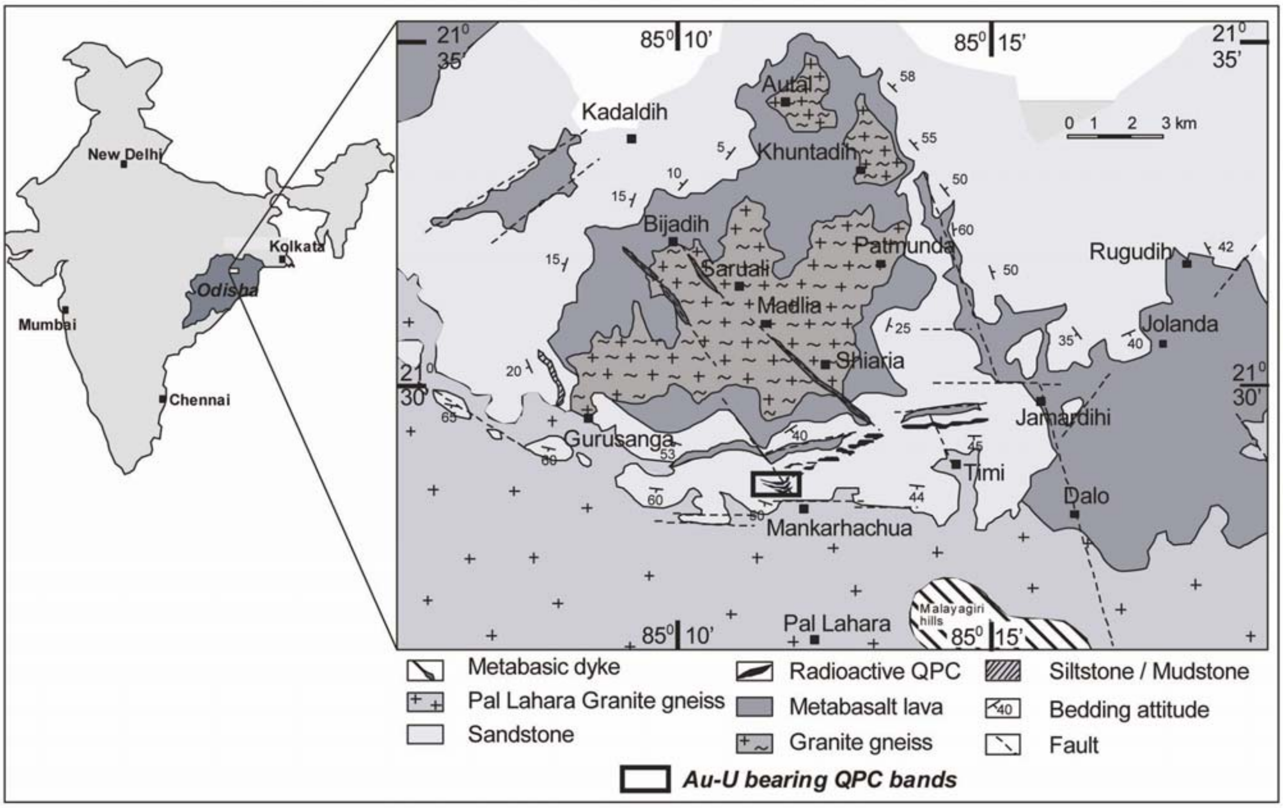

Figure 1. Geological map of Mankarhachua area showing location of gold–silver-bearing radioactive quartz-pebble conglomerate (QPC) horizons in the rectangular area (T.S. No. 73G/2, 3, 6 & 7).

(Figure 1). Significant radioactivity is recorded in three sub-parallel uraniferous QPC horizons inter-layered with mildly metamorphosed, pebbly to medium-grained, recrystallized, massive, and trough and ripple cross-stratified sandstones for a strike length of over 2 km. The bedding planes are dipping moderately (45–55°) towards south. These radioactive bands are delineated for more than 225 m strike length continuously and continue further eastward intermittently over a strike length of 2.06 km. The thickness of individual radioactive QPC bands varies widely; the middle one is the thickest (4.50–12.25 m), the southernmost thinnest (1.5–5.30 m) and the northernmost is of intermediate thickness (3.0–8.5 m). The cumulative thickness of radioactive QPC and intervening recrystallized sandstone is 19 m. The size of the rounded clasts varies widely from 2 to 10 cm in diameter. The size of the clasts increases as the thickness of QPC band increases.

The QPCs are matrix-supported, non-graded, massive with concave, upward lower bounding surface and flat to wavy upper bounding surface. They contain well-rounded to sub-angular pebbles of vein quartz, black, green and yellowish white chert, banded chert and smoky quartz set in a predominant very coarse sandy matrix with subordinate micaceous (sericitic, fuchsitic and chloritic) minerals. Pebbles constitute 55–65% and matrix constitutes 35–45% by volume without any other cementing component. Polished thin sections of QPC samples show clasts of mono- and poly-crystalline vein-quartz, fine quartz arenite/quartz-wacke and rarely carbonaceous siltstone. The matrix is constituted by assorted assemblage of arenaceous clasts of very fine to very coarse sands of quartz and heavy minerals (meta-quartz-wacke in composition). The heavy mineral population constitutes abundant detrital rounded grains of pyrite, arsenopyrite (Figure 2 *a* and *c*), uraninite, uranothorite, thorite, monazite, zircon, rutile, rare magnetite, chromite and fine rounded uraninite trapped in profuse carbonaceous matter[11]. Secondary uranium mineral encrustations, altered minerals after uraninite have also been identified by X-ray diffraction (XRD) and scanning electron microscopic (SEM) studies.

In the samples collected from the bed rock exposed on the surface, the auriferous nature of the radioactive QPC horizons was first identified in the matrix by the electron probe micro-analytical (EPMA-CAMECA SX-100) studies using wavelength dispersive spectrometry (WDS) at the Central Facility of the Department of Geology and Geophysics, IIT, Kharagpur. SEM studies have been carried out on the polished thin sections of the uraniferous QPC matrix. Carbon-coated samples were studied under TESCAN VEGA LSU SEM facility at the UGC-CAS Laboratory, Presidency University, Kolkata. Samples were run under the accelerating voltage of 15 kV. The backscattered electron image (BSE) of gold grains

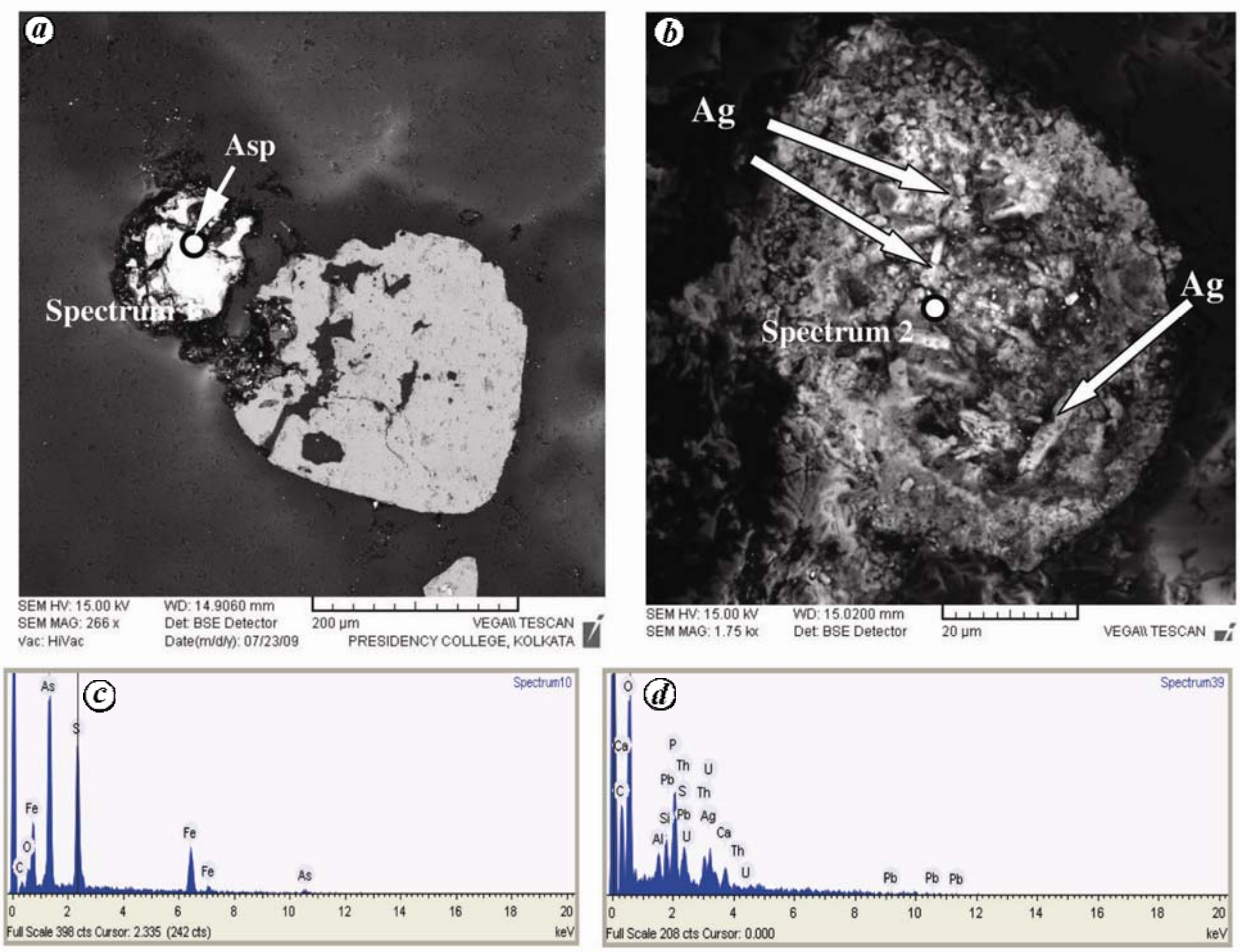

Figure 2. ***a***, Backscattered electron (BSE) image of bright arsenopyrite grain (Asp) with irregular outline in association with the detrital rounded and broken pyrite grain (Py) in uraniferous QPC matrix of Mankarhachua area. ***b***, BSE image of rounded highly altered monazite grain replaced by bright platy silver-bearing minerals (Ag); this is an evidence of the possible effect of post-depositional modification. ***c***, Energy dispersive spectrum (EDS) of the circled area of the arsenopyrite grain shown in (***a***). ***d***, EDS of the circled area of one of the grains of platy Ag-rich minerals shown in (***b***).

exhibits an irregular broken outline. The surface of these grains is otherwise smooth, except for some polishing scratches. The highly irregular outline of some parts of the gold grains may be due to stretching of the malleable gold grains during diagenesis and lithification (Figure 3 *b* and *c*). The energy dispersive spectrometric (EDS) semi-quantitative analyses of gold grains suggest native nature of the gold with very less amount of association with other elements (viz. Ag).

The silver-bearing minerals of the QPC occur as bright, platy, randomly oriented minerals in skeletal, highly altered monazite grains. EDS spectrum suggests presence of highly altered U–Th-bearing phosphate minerals with rounded outline being replaced by the platy, silver-bearing minerals (Figure 2 *b* and *d*). However, the mineral phases of the silver-rich platy grains are not known.

Au, Ag and PGE abundances in the Mankarhachua radioactive QPC matrix have been estimated by chemical analysis at the AMD Laboratory in Hyderabad. The spatial distribution of gold was studied by collecting a few bed-rock samples, which were processed by pre-concentration with tellurium and estimation and determination by graphite furnace-atomic absorption spectrometer (GF-AAS). The above procedure was validated by analysing suitable certified reference materials (CRMs; MA-1b Au-17 ppm, SARM-53 Au 3.99 ppm). The instrumental detection limit and method detection limits are 4 and 10 ppb respectively, with 10% error. Ag was estimated by inductively coupled plasma-mass spectrometer (ICP-MS) using suitable CRMs. Platinum Group Elements (PGEs) were analysed by nickel sulphide fire assay followed by ICP-MS (model: Micromass Platform-XS) analysis. More samples were analysed for gold and silver only, using graphite furnace-flame ASS technique with a detection limit of 15 ppb and determination limit of 50 ppb for Au and 4 and 15 ppb for Ag respectively, at the Chemistry Laboratory of AMD in Jamshedpur. However, the accuracy of the estimates with respect to CRMs could not be determined out in this laboratory due to non-availability of CRM solutions. Despite this shortcoming, data on some common samples (three samples) analysed by both the laboratories were found to be similar.

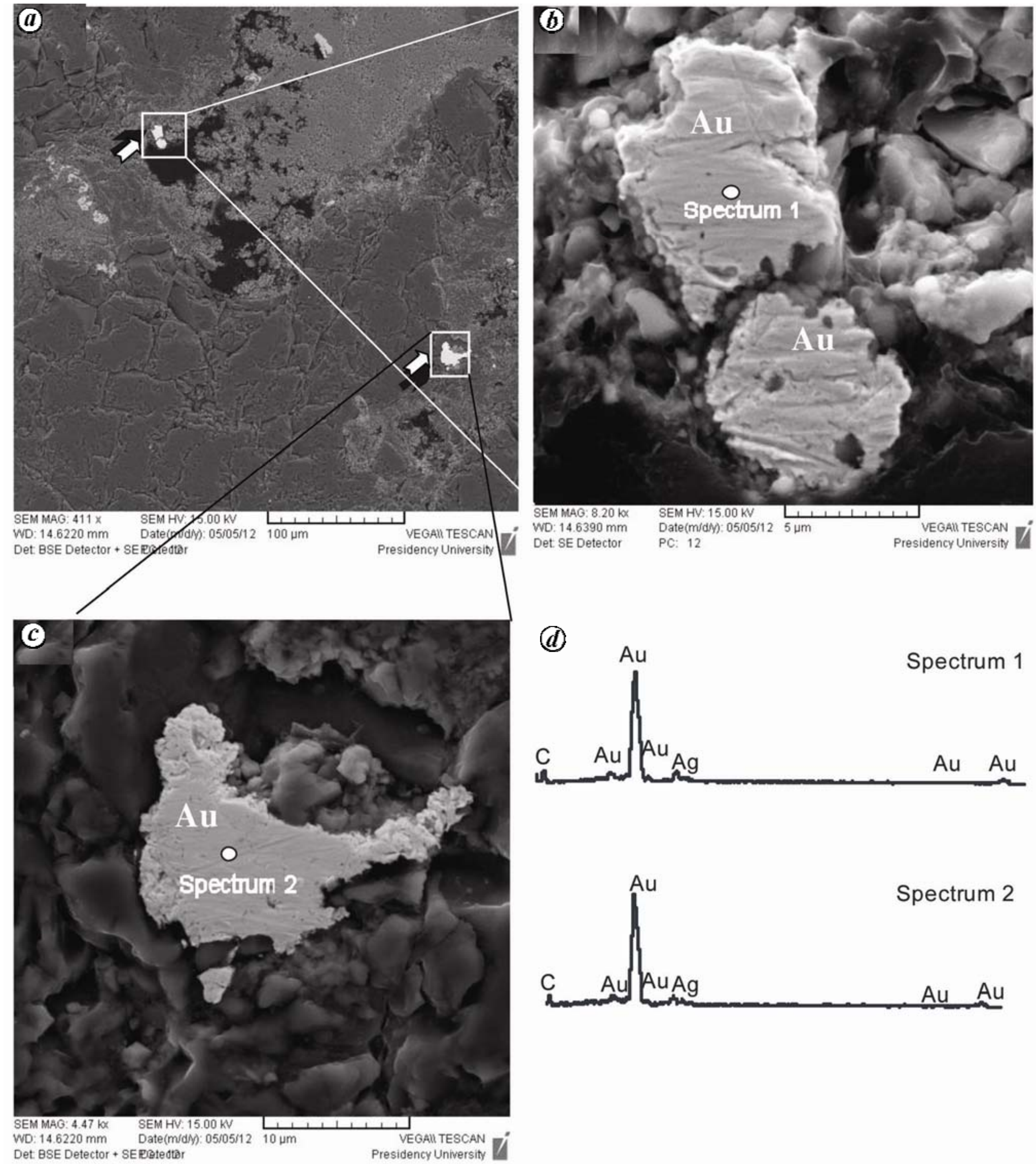

Figure 3. ***a***, Fused secondary electron (SE) and BSE images of gold-bearing uraniferous QPC matrix of Mankarhachua area; two rectangular areas marked exhibit bright irregular outline of detrital gold grain. ***b***, Magnified secondary electron (SE) image of the rounded and broken outline of two detrital grains of gold. Note the hackly nature of the outline of the gold. ***c***, Magnified fused SE and BSE image of another detrital grain of gold. Highly irregular and stretched outline of the grain is possibly because of stretching due to malleability of gold in response to the post-depositional diagenesis and lithification of QPC. ***d***, EDS spectra of the white spotted areas of gold grains shown in (***b***) and (***c***). Spectra show native nature of the gold grains depicted by absence of other elemental peaks.

The results exhibit, significant presence of gold and silver in QPC-hosted uranium mineralization zone at Mankarhachua area (Table 1). The gold values range from 15 ppb to as high as 29 ppm with an average of 5.04 ppm, which is significantly above the crustal abundance of 2 ppb for 11 radioactive QPC samples and one sample from intervening sandstone horizon[1,12]. The samples analysed at the Chemistry Laboratory of AMD in Jamshedpur,

Table 1. Chemical analysis of gold and silver vis-à-vis radiometric assay values from different QPC bands, Mankarhachua area

		Parts per billion		Percentage				
Sample no.	Lithology	Au	Ag	eU_3O_8	U_3O_8	$RaeU_3O_8$	ThO_2	K
MK-28	Pebbly sandstone (eastern extension)	139	94	0.013	<0.010	–	0.017	<0.5
MK-44	Ferruginized QPC, Ratab	27	20	28 ppm	–	7 ppm	37 ppm	1.1
MK-45	Ferruginized QPC, Ratab	15	<10	–	–	–	–	–
MK-48	Radioactive QPC, lower band	5 ppm	3010	0.157	0.021	0.129	0.068	–
MK-50	Radioactive QPC, lower band	29 ppm	1390	0.143	0.048	0.134		
MK-56	Radioactive QPC, lower band	12 ppm	2150	0.027	<0.010	0.018	0.020	<0.5
MANK-60	Radioactive QPC, middle band	73	43	34 ppm		14 ppm	42 ppm	0.5
MANK-70*	Radioactive QPC, lower band	17 ppm	4.6 ppm	0.125	0.013	0.093	0.078	–
MANK-71*	Radioactive QPC, lower band	< 0.1 ppm	0.3 ppm	0.030	0.010	0.018	0.026	1.0
MANK-72*	Radioactive QPC, lower band	< 0.1 ppm	0.3 ppm	0.018	<0.010	0.010	0.017	<0.5
MANK-60	Radioactive QPC, middle band	73	43	34 ppm		14 ppm	42 ppm	0.5
MANK-74	Radioactive QPC, lower band	7 ppm	684	0.143	0.047	0.101	0.094	–
MANK-75*	Radioactive QPC, lower band	1.3 ppm	0.8 ppm	0.027	<0.010	0.018	0.020	<0.5
MANK-76*	Radioactive QPC, lower band	< 0.1 ppm	<0.1 ppm	32 ppm	–	17 ppm	37 ppm	0.5
MANK-81	Radioactive sandstone, between lower and middle band	28	1555	61 ppm	–	17 ppm	101 ppm	<0.5
MANK-90	Radioactive QPC, lower band (western end)	128	87	0.013	<0.010	0.003	0.021	0.5
MANK-91*	Radioactive QPC, middle band	< 0.1 ppm	0.1 ppm	58 ppm	–	12 ppm	102 ppm	<0.5
MANK-92*	Radioactive QPC, middle band	< 0.1 ppm	<0.1 ppm	72 ppm	–	39 ppm	73 ppm	<0.5
MANK-93	Radioactive QPC, middle band	72	80	0.012	<0.010	0.004	0.017	0.5
MANK-96	Radioactive QPC, lower band	7 ppm	743	0.068	0.017	0.015	0.016	–

*Marked samples are analysed in the Chemistry Laboratory, AMD, Jamshedpur; ppb, parts per billion; ppm, parts per million.
All data for Au and Ag are in ppb, except otherwise mentioned.
All data for eU_3O_8, U_3O_8, $RaeU_3O_8$, ThO_2 and K are in percentage, except otherwise mentioned.

Table 2. Chemical analysis of PGE vis-à-vis radiometric assay values from different QPC bands, Mankarhachua area

		Parts per billion					Percentage				
Sample no.	Lithology	Pt	Pd	Ir	Rh	Ru	eU_3O_8	U_3O_8	$RaeU_3O_8$	ThO_2	K
MK-28	Pebbly sandstone (eastern extension)	<10	<10	<10	<10	<10	0.013	<0.010	–	0.017	<0.5
MK-44	Ferruginised QPC, Ratab	11	<10	<10	<10	<10	28 ppm	–	7 ppm	37 ppm	1.1
MK-45	Ferruginised QPC, Ratab	<10	<10	<10	<10	<10	–	–	–	–	–
MK-48	Radioactive QPC, lower band	13	<10	<10	<10	<10	0.157	0.021	0.129	0.068	–
MK-50	Radioactive QPC, lower band	20	<10	24	<10	<10	0.143	0.048	0.134		
MK-56	Radioactive QPC, lower band	60	32	13	31	78	0.027	<0.010	0.018	0.020	<0.5
MANK-60	Radioactive QPC, middle band	46	<10	<10	<10	<10	34 ppm		14 ppm	42 ppm	0.5
MANK-74	Radioactive QPC, lower band	83	<10	<10	<10	16	0.143	0.047	0.101	0.094	–
MANK-81	Radioactive Sandstone, between lower and middle band	27	<10	<10	10	39	61 ppm	–	17 ppm	101 ppm	<0.5
MANK-90	Radioactive QPC, lower band (western end)	44	<10	10	<10	49	0.013	<0.010	0.003	0.021	0.5
MANK-93	Radioactive QPC, middle band	79	<10	14	17	67	0.012	<0.010	0.004	0.017	0.5
MANK-96	Radioactive QPC, lower band	53	<10	13	12	57	0.068	0.017	0.015	0.016	–

also reported gold values varying from < 0.1 ppm to as high as 17 ppm (n = 7). Of these seven samples, two contain more than 0.1 ppm gold (17 and 1.3 ppm).

Significant abundance of silver is also recorded, which ranges from <10 ppb in one sample to as high as 3010 ppb with an average of 896 ppb (n = 11, excluding one sample value which is <10 ppb). The average silver value is about 16 times the crustal abundance of silver (56 ppb)[12].

The total PGE content (∑PGE) varies from <10 to 177 ppb (Table 2). Most of the samples recorded anomalous concentration for platinum (Pt: <10–83 ppb, av. 44 ppb; crustal abundance 3.7 ppb), ruthenium (Ru: <10–78 ppb, av. 51 ppb; crustal abundance 1 ppb) and iridium (Ir: <10–24 ppb, av. 15 ppb; crustal abundance 1 ppb), while a few samples (four out of 12 samples), showed anomalous concentration of rhodium (Rh: <10–31 ppb, av. 18 ppb; crustal abundance 0.7 ppb) and palladium (Pd: <10–32 ppb; only one out of 12 samples yielded >10 ppb value [32 ppb]; Table 2).

Correlation was studied between the associated elements (Table 3). From the raw data on precious metals and the correlation matrix of these metals with associated elements, the following inferences on the distribution and

Table 3. Correlation coefficient matrix of the associated elements of the Au + Ag + PGM + U-bearing QPC of Mankarhachua area

	U	Th	Cr	Ni	Cu	Ru	Rh	Pd	Pt	Ir	Ag	Au
As	0.58	–0.34	–0.85	0.09	0.22	0.15	–0.24	0	–0.47	0.05	0.9	0.61
Au	0.69	0.88	0.26	0.06	0.07	–0.02	0.2	0.26	0.01	0.9	0.44	
Ag	0.32	0.42	0.42	0.02	–0.03	0.13	0.33	0.42	–0.09	0.2		
Ir	0.46	0.71	0.15	–0.2	–0.15	0.07	0.13	0.08	0.02			
Pt	0.4	0.17	–0.53	0.52	0.63	0.62	0.43	0.26				
Pd	0.03	0.13	0.31	–0.05	–0.02	0.58	0.94					
Rh	–0.01	0.07	0.23	–0.11	–0.04	0.74						
Ru	–0.09	–0.15	–0.25	–0.19	–0.05							
Cu	0.74	0.42	–0.32	0.98								
Ni	0.72	0.44	–0.27									
Cr	–0.06	0.2										
Th	0.85											

control on gold and silver mineralization in Mankarhachua QPC have been drawn:

1. From the data shown in Table 1, it is observed that the high concentration of gold is hosted by the radioactive sub-parallel QPC bands in Mankarhachua occurrence.
2. The higher gold and silver values are mainly restricted to the lower QPC horizon (the northernmost band). This band also has highest uranium content among the three sub-parallel QPC bands.
3. From the correlation matrix it is observed that there is a positive correlation between gold and uranium ($r = 0.69$), and gold and thorium values ($r = 0.88$). Gold shows poor correlation with silver ($r = 0.44$) as well as copper ($r = 0.07$) and nickel ($r = 0.06$).
4. Arsenic values have good correlation with silver ($r = 0.9$), while a moderate correlation exists with gold ($r = 0.61$). Arsenic has poor correlation with all other elements.

From the above SEM-EDS studies and chemical analytical data, it is observed that gold is not associated with silver. Although arsenic is commonly present in Mankarhachua QPC matrix, gold showed only moderate correlation with arsenic (generally gold gets associated with arsenopyrite). Gold is also not associated with Cu and Ni, negating its derivation from basic sources. Gold is in native state and occurs as detrital grains derived possibly from ultramafic source (as indicated by good correlation with Ir [$r = 0.9$]). Its good correlation with thorium and uranium-bearing heavy detritus in the lower part of the lower QPC band indicates a placer mode of concentration of gold in the QPC matrix. The typical replacement texture, strong correlation of silver with arsenic and poor correlation with all other elements are noteworthy and suggest a strong association of silver with arsenopyrite or its occurrence as silver arsenides. This is an indication of a possible epigenetic hydrothermal origin of silver in association with arsenic-bearing minerals.

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