‘Indicator’ carbonaceous phyllite/graphitic schist in the Archean Kundarkocha gold deposit, Singhbhum orogenic belt, eastern India: Implications for gold mineralization *vis-a-vis* organic matter

P R SAHOO and A S VENKATESH*

Department of Applied Geology, Indian School of Mines, Dhanbad 826 004, Jharkhand, India.

**Corresponding author. e-mail: asvenkatesh@hotmail.com*

Carbonaceous rocks in the form of graphitic schist and carbonaceous phyllite are the major host rocks of the gold mineralization in Kundarkocha gold deposit of the Precambrian Singhbhum orogenic belt in eastern India. The detection of organic carbon, essentially in the carbonaceous phyllite and graphitized schist within the Precambrian terrain, is noted from this deposit. A very close relationship exists between gold mineralization and ubiquitous carbonaceous rocks containing organic carbon that seems to play a vital role in the deposition of gold in a Precambrian terrain in India and important metallogenic implications for such type of deposits elsewhere. However, the role played by organic matter in a Precambrian gold deposit is debatable and the mechanism of precipitation of gold and other metals by organic carbon has been reported elsewhere. Fourier transform infrared spectroscopy (FTIR) results and total organic carbon (TOC) values suggest that at least part of the organic material acted as a possible source for the reduction that played a significant role in the precipitation of gold. Lithological, electron probe analysis (EPMA), fluid inclusions associated with gold mineralization, Total Carbon (TC), TOC and FTIR results suggest that the gold mineralization is spatially and genetically associated with graphitic schist, carbonaceous phyllite/shale that are constituted of immature organic carbon or kerogen. Nano-scale gold inclusions along with free milling gold are associated with sulfide mineral phases present within the carbonaceous host rocks as well as in mineralized quartz-carbonate veins. Deposition of gold could have been facilitated due to the organic redox reactions and the graphitic schist and carbonaceous phyllite zone may be considered as the indicator zone.

1. Introduction

Commonly gold occurrences that are associated with organic carbonaceous and graphitic material have been reported from Paleozoic, Mesozoic, and Tertiary periods (Springer 1985; Mastalerz *et al.* 2000; Bierlein *et al.* 2001; Craw 2002; Pitcairn *et al.* 2005; Williams 2007). Black shale rock complexes are considered to have great potential as host rocks of noble metals (Meyers *et al.* 1990). Such

complexes host gold deposits in North-East Russia (Natalka, Mayskoe, Nezhdaninskoye), Australia (Bendigo, Ballarat), Alaska (Juno), California (Maser Lode), and in many other belts. Substantial Au concentrations have been reported in carbonaceous shales within Zechstein copper deposit, Poland (Kucha 1982). In some of the Au deposits, the carbonaceous host rocks are closely associated with gold mineralization and have been considered ‘Indicator’ litho-units (Springer

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1985; Bierlein *et al.* 2001; Craw 2002; Król *et al.* 2009).

The Singhbhum Craton (3.51 Ga; Mukhopadhyay *et al.* 2008) includes the Banded Iron Formation (BIF) associated with mafic, komatiitic ultramafic rocks and meta volcano-sedimentary units (Saha 1994; Mahadevan 2002). The gold mineralization occurs within the Archean Badampahar–Gorumahisani schist belt (ca. 3.12 ± 0.01 Ga; Ghose 1996) representing the Iron Ore Group. The lithological sequence associated with gold mineralization in and around Kundarkocha that occurs within the Precambrian Singhbhum orogenic belt (figure 1) is talc-serpentine-chlorite schist, fuchsite-quartzite, carbonaceous phyllite/slate, graphitic schist, and quartz-carbonate veins (figure 2a–c). Gold mineralization at Kundarkocha is associated with quartz-carbonate-sulfide veins and is exposed

on the surface as well as in the underground mine-faces. However, the occurrence of graphitic schist is observed in the subsurface mining face where it occurs parallel to the auriferous quartz reef (figure 1). Although organic matter has been documented from some gold deposits, its role in the genesis of gold mineralization is the subject of ongoing debate (Springer 1985; Mastalerz *et al.* 2000; Bierlein *et al.* 2001; Craw 2002; Pitcairn *et al.* 2005; Król *et al.* 2009). One of the mechanisms could be explained by the association of gold with the sulfidised organic matter (Meyers *et al.* 1990). Organic material in the form of total organic carbon is reported from Kundarkocha gold deposit in this research work. The organic activity in gold deposition has not been reported from any Indian gold deposits studied so far and we report a close relationship with gold mineralization and organic carbon in the form of immature kerogen (degraded

Figure 1. Generalized geological map of Kundarkocha area (modified after Banerjee and Thiagarajan 1965) of Precambrian Singhbhum orogenic province showing an inset of the geology of a portion of the underground mine.

Figure 2. (a) Sample of a gold bearing folded carbon-rich cherty phyllite, (b) graphite schist from the mineralized zone, (c) photomicrograph showing syn-sedimentary carbonaceous material following the foliation plane of talc-chlorite schist (crossed nicols), (d) coexisting phases of arsenopyrite-pyrite-pyrrhotite assemblage from mineralized quartz vein along the graphitic schist zone, (e) BSE image of zoned arsenopyrite with an arsenic rich core and gold inclusion along the fractures, and (f) BSE image of zoned-arsenopyrite exhibiting invisible gold distribution.

kerogen), a part of which was altered to impure graphite.

Most of the studied samples are a physical mixture of carbonaceous phases in variable stages of structural ordering that differ in their morphology, textural properties, and reflectivity and these heterogeneous carbonaceous phases, may be classified as carbonaceous phyllite/slates, graphitic schist, and kerogen. Invisible gold, nano-scale inclusions of gold within the unzoned, zoned-sulfide phases, and visible gold in the form of nuggets forming main lode are all present within the carbonaceous rocks as well as in the discrete mineralized quartz-carbonate-sulfide veins (Sahoo 2012; Hazarika *et al.* 2013; Sahoo and Venkatesh 2013). The sulfide phases containing visible forms of gold (figure 2d and e) and invisible gold (figure 2f) are inter-stratified with the carbonaceous units. Integrated petrographic studies of the host rocks, ore textures, cross-cutting relationships of the mineralized veins, and mineral assemblages in Kundarkocha suggest that a majority of gold mineralization is associated with the early stage sulfides (pyrite and arsenopyrite). In the present study, attempts have been made to (a) understand the role of carbonaceous units in the genesis of gold mineralization, (b) study the nature of carbonaceous rocks as to whether they are of organic or inorganic origin, and (c) understand the implications of the close spatial association of 'indicator' graphitic schist and carbonaceous rocks with the gold mineralization.

2. Geological overview and nature of gold mineralization

The geology around Kundarkocha comprises green-schist to lower amphibolite facies metamorphic rocks, intruded by gabbro, ultrabasic rocks, granites, and dolerites (Saha 1994; Mahadevan 2002) (figure 1). The mineralized quartz-carbonate-sulfide veins (figure 2d) are emplaced within the carbonaceous phyllite, graphitic schist, talc-chlorite-serpentine schist, and fuchsite schist gold is occasionally found as nuggets within these. Sulfides and associated gold mineralization occur as veins and stringers along the stratification planes, foliation, and fractures (Sahoo *et al.* 2010). Gold mineralization is associated with grey to black and rarely with green chert inter-banded with carbonaceous phyllite and fuchsite bands, smoky/blue quartz and talc-chlorite-schist and shows conformity with the planar features such as bedding planes. The field relationships and photo-microscopic features within carbonaceous litho units are shown in figures 2(c) and 3. The graphitic zone is prominent along the interface between the chlorite schist and carbonaceous phyllite (figure 1). This is a promising zone for gold and associated sulfides. The carbonaceous rocks acted as the reducing agent for gold precipitation and are hence considered to be an indicator zone for mineralization.

In the area adjoining Kundarkocha area, six tentative anomalous zones have been delineated which

Figure 3. XRD peaks showing ankerite, graphite, calcite and associated pyrite within the carbonaceous host rock.

contain a number of mineralized quartz-carbonate veins (figure 1). The ore body characteristics have been discussed by some of the earlier workers, viz., Ghose (1996), Ziauddin and Narayanaswami (1974), Sahoo *et al.* (2010), Gupta (2010), Singh *et al.* (2011), Sahoo (2012), Hazarika *et al.* (2013) and the exploration aspects have been reported by various organizations including Geological Survey of India, Mineral Exploration Corporation Limited, and the lease holder M/s Manmohan Mineral Industries Private Limited. Two major auriferous quartz veins of 200 m strike length each have been established besides numerous auriferous small quartz veins at Kundarkocha. Presence of old workings/shafts/prospecting pits surrounding the area reveal ancient mining history in the area. Non-consistent occurrence of the mineralized zone along the strike length, supported by the presence of old workings/shafts/prospecting pits surrounding Kundarkocha is suggestive of the extension of the main ore body. The smaller prospects could be the detached extensions of the ore body or ore

shoot zones controlled by structural complexity of the area. A number of auriferous veins at different levels with variable assay values have been identified in the underground exploratory work. Sometimes the assay value reaches up to 8–14 g/t. For the purpose of estimation of reserves, strike lengths of 250 m and depth up to fourth level (each level having a thickness of 30 m) have been considered for both the lodes. Beyond the first level, all the levels are developed at a vertical interval of 30 m. The total geological reserve calculated is around 63,600 tonnes for two lodes; each having a strike length of 250 m up to the depth of 120 m and average thickness of 0.8 m.

3. Organic carbon characterization

3.1 TC and TOC, and FTIR analyses

For the determination of total carbon and total organic carbon (TOC), selected samples including graphitic schist, carbonaceous phyllite, slate and chlorite-schist having carbon rich veins were finely powdered and treated with concentrated HCl for 20 hours for the total removal of carbonate carbon in the form of CO₂ (ASTM International 2004). A constant temperature of 50°C was maintained during the heating of the powdered samples, which were regularly stirred to ensure dissolution of carbonates into acid in the Teflon beaker. Then the decarbonated, moistened carbonaceous rock was repeatedly washed with distilled water to ensure the total removal of the carbonate carbon and the residue was dried in an oven at a constant temperature of 50°C for a period of 2 hrs. After the total removal of CO₂, one set of decarbonated powdered sample and another set of untreated dried sample powder were analyzed using Vario El III, CHNSO Elemental Analyzer at Indian School of Mines. Results of the analysis of untreated sample indicate the total carbon whereas those of the acid treated samples are total organic carbon after decarbonation.

Fourier Transform Infrared (FTIR) and Infra Red (IR) analysis techniques are of use in geological studies for mineralogical, petrological, and fluid inclusion characterization. FTIR technique is used in coal and organic petrological studies to understand the chemical structure of macerals in coal and kerogens in petroliferous rocks and other rocks (Landais 1995; Yule *et al.* 2000; Pitcairn *et al.* 2005). For FTIR analysis of carbon, the carbonaceous rocks were finely powdered and subjected to hot HCl→HF→HNO₃ digestion for 24 hours for the removal of silicates and carbonates and sulfides. Then the moistened concentrate was filtered repeatedly with distilled water for 5–6 times and

the washed residue was dried in an oven at constant temperature of 50°C. A small fraction of the carbonaceous concentrate was added with KBr and thin pellets were prepared for FTIR analysis (Russell 1987). IR spectra were recorded using Perkin Elmer FTIR spectrometer at Indian School of Mines. The IR spectra were manipulated with Spectrum 2000 software and reported in transmittance units as function of wave number (cm^{-1}) in the 4000–370 cm^{-1} range. The spectral band assignment was chosen after Pitcairn *et al.* (2005) and Ibarra *et al.* (1996).

FTIR analysis on carbon-bearing rocks like graphitic schist, carbonaceous phyllite-slate and carbonaceous layers part of the chlorite schist shows distinct peaks (figure 4) for C–H stretch at 2700–3000 cm^{-1} range, carbon peaks at 1025–1035 cm^{-1} , carbonate peaks at 1450 cm^{-1} , C=O at 1700 cm^{-1} , and water peaks at 1615 cm^{-1} and 1950 cm^{-1} . Classic kerogen profiles with spectral lines at 3620 and 3400 cm^{-1} from OH molecule stretching, 2927 and 2865 cm^{-1} related to symmetric and asymmetric CH_2 and CH_3 , and 1705 and 630 cm^{-1} related to C=O and C=C bonds, have been noted respectively (figure 4). The peaks at 3620, 3400, 2925, 2685, 1705, and 1630 cm^{-1} signify the reduced peaks, indicating the progressive loss of volatile elements such as H_2O , OH, CH_2 , and CH_3 , and restructuring of the increasingly carbon-rich unit, through the alteration of C=O and C=C bonds that occur during graphitization (Pitcairn *et al.* 2005).

The origin of graphite in a low temperature condition may be explained in two ways. In nature, graphite can be formed in two processes, i.e., by metamorphic conditions (Landis 1971; Wada *et al.*

1994; Sanyal *et al.* 2009; Mishra and Bernhardt 2009) and by hydrothermal deposition from a highly carbonic rich fluid composition (Dissanayake 1981; Jedwab 1984; Craw 2002; Pitcairn *et al.* 2005; Luque *et al.* 2009). Graphite formation in a metamorphic terrain is considered to be a progressive temperature dependent transition from amorphous kerogen to crystalline graphite with the gradual crystallinity of the carbonaceous material (Landis 1971; Buseck and Bo-Jun Huang 1985; Wilson and Rucklidge 1987; Wilson and Zentilli 1999). It is proposed that a part of the precursor carbonaceous unit has been converted to graphitic schist. In the graphitic zone, discrete fine grained graphite is present which has been identified from the XRD peaks of the sample as suggested by Landis (1971).

3.2 Fluid inclusion characteristics and Raman spectroscopy

Attempts have been made to characterize the mineral bearing fluid of the gold deposit to understand whether organic carbon has any role in controlling the composition of the mineralizing fluid. Three types of fluid inclusions are noted from the mineralized quartz veins. Among them the Type-IIa inclusions are predominant and carbonic in nature. The fluid inclusions are limited as most of them are re-crystallized and affected by local shearing. Most of the preserved inclusions are aqueous biphasic and carbonic (figure 5) that homogenize at a temperature range of 160°–290°C. Melting temperature (T_m) of the aqueous inclusions ranges from –5 to –21°C and the salinity ranges from 8.5 to 12.35. For carbonic inclusions, T_m ranges from –47 to –62°C that corresponds to a CO_2

Figure 4. FTIR peaks of carbon-bearing rocks showing distinct graphitic peaks and kerogen functional groups. The samples S0, S23, S13 are graphitized whereas S21 is carbon-bearing chlorite schist occurring along the mineralized quartz vein.

rich phase. The salinity of the carbonic fluid ranges from 4.5 to 8.9. The aqueous inclusions (5–15 μm) are larger in size than the carbonaceous inclusions (2–6 μm). These fluid inclusions have been further characterized and corroborated for identifying the carbonic phases using Laser Raman Spectrometry. Raman spectroscopy has been widely used for fluid inclusion analytical techniques (Roedder 1990; Burke 2001; Morizet *et al.* 2009). Raman spectroscopy was performed using Nicolet Almega XR of Thermo Electron Corporation with the OMNIC 7.3 version software at Indian Institute of Technology, Bombay. The Raman system calibrations and methodology were used as per Pandalai *et al.* (2008). Raman spectroscopy of the carbonaceous inclusions revealed the presence of graphite, CH_4 , and CO_2 phases (figure 5). The intensity of the carbonic phases is not so high as compared to the highly carbonic phases documented elsewhere. Based on the fluid inclusion characteristics, TOC, FTIR, and Laser Raman Spectrometry analyses, it may be inferred that the transformation of graphite from the organic carbon-rich material could have resulted due to the interaction between the carbonaceous material and hydrothermal fluid (figure 2). Further, there are evidences of a strong interaction of the hydrothermal fluid with the wall rock resulting in the development of wall rock alteration zones like zones of chloritization, carbonitization, sericitization, and serpentinization (figure 6).

4. Archean gold mineralization associated with organic carbon

Organic activity in mineralization during Archean era is one of the debatable topics in geology. However, significant organic components/organic activity associated with gold mineralization have been reported from Archean black shales/carbonaceous rocks (western Lachlan Orogen, Victoria, Southeast Australia; Witwatersrand basin, South Africa Barberton greenstone belt, South Africa). Though the origin of carbon, whether organic or inorganic or a combination of both is quite debatable, two possible hypotheses in the study area may be considered; (i) the subaerial precipitation of carbon formed due to the combustion of volcanic gases containing hydrocarbon and carbon monoxide under favourable thermal conditions and (ii) formation of carbon as a fumarolic deposit towards the close of the volcanic activity by breakdown of gases permeating the sediments of volcanic dust associated with the flows (Dunn 1929).

To understand the constraints on the genesis and nature of the carbon bearing rocks in this Archean terrain, carbon content was characterized as carbonate carbon and organic carbon within the mineralized carbonaceous host rocks. Graphitic schist is found to contain higher amounts of TOC than other carbonaceous rocks and organic carbon layers have also been noticed within the foliation planes (figure 2c) of chloritic schist besides carbonate

Figure 5. Carbonaceous fluid inclusions and their corresponding Raman shifts showing methane and graphite peaks (x-axis: Raman Shift (cm^{-1}); y-axis: Raman Intensity). The carbonic inclusions indicate the strong reducing condition which favoured the precipitation of gold. Graphite was formed by the reaction between CH_4 and CO_2 .

(inorganic) veins of ankerite and calcite (figure 3). The black graphitic material (impure graphite) in the mineralized zone is very fine, noncrystalline in habit, and hard with a moderate reflectivity. Graphite formation in a metamorphic terrain is considered to be a progressive, temperature dependent transition from amorphous kerogen to crystalline graphite with the gradual crystallinity of the carbonaceous material (Buseck and Bo-Jun Huang 1985; Wilson and Rucklidge 1987). From the nature of graphitic material and carbon content, it is suggested that the kerogen was devolatilized variably by the hydrothermal fluids resulting in partial development of a graphitic zone which is restricted to proximal zone. Fluid inclusion characteristics along with Raman spectrometric data suggest that carbonic and aqueous fluid activity probably aided the transport and subsequent phase-wise concentration of Au. Sulfidation in a hydrothermal system has greater implication for mineralization as the interaction between rocks and hydrothermal fluids causes metal leaching and deposition (Kettler *et al.* 1990). Williams (2007) has shown the occurrence of gold along with graphite and suggested that it could have been formed by the decarbonization process of graphite which is a characteristic feature of hydrothermal alteration that facilitated removal of CO₂ from

graphite, a process which is associated with bleaching and the development of bedding-parallel bands of host rocks (figure 2c) as given below.

Fourier Transform Infrared (FTIR) and Infra Red (IR) analysis techniques are of use, albeit in limited extent, in geological studies for mineralogical, petrological, and fluid inclusion characterization. FTIR technique is used in coal and organic petrological studies to understand the chemical structure of macerals in coal and kerogens in petroliferous rocks and other rocks (Landais 1995; Yule *et al.* 2000; Pitcairn *et al.* 2005). Here, we attempt FTIR analysis on carbon-bearing rocks like graphitic schist, carbonaceous phyllite-slate, and carbonaceous layers within chlorite schist that show distinct peaks (figure 4) for C–H stretch at 2700–3000 cm^{−1}, range, carbon peaks at 1025–1035 cm^{−1}, carbonate peaks at 1450 cm^{−1}, C=O at 1700 cm^{−1}, and water peaks at 1615 cm^{−1} and 1950 cm^{−1}. Classic kerogen profiles with spectral lines at 3620 and 3400 cm^{−1} from OH molecule stretching, 2927 and 2865 cm^{−1} related to symmetric and asymmetric CH₂ and CH₃, and 1705 and 630 cm^{−1} related to C=O and C=C bonds, have been noted respectively (figure 4). The peaks at

Figure 6. Photomicrographs of (a) calcite and quartz veins within the interface zone of the graphitised zone and the chlorite-schist; (b) sericitization as a part of wall rock alteration zone; (c) very fine ankerite veins in addition to the calcite vein within the schistose rocks; and (d) serpentinization of the ultramafic rock units observed in the underground mine faces.

3620, 3400, 2925, 2685, 1705 and 1630 cm^{-1} signify the reduced peaks, indicating progressive loss of volatile elements such as H_2O , OH, CH_2 and CH_3 , and the restructuring of the increasingly carbon-rich material, through the alteration of $\text{C}=\text{O}$ and $\text{C}=\text{C}$ bonds that occurs during graphitization (Pitcairn *et al.* 2005).

5. Possible depositional conditions of gold

The presence of both native and invisible gold along with microscale inclusions of gold within sulfide minerals envisages complicated evolution of gold (Deditius *et al.* 2011). These forms are spatially and genetically different from each other and might have formed at different stages and from compositionally different mineralizing fluid (Sahoo 2012). Visible gold (figure 2d and e) occurs in quartz veins as well as within carbonaceous rocks. Gold-bearing zoned-arsenopyrite grains with a loellingite core region occur within the carbonaceous rocks (Sahoo and Venkatesh 2013). Loellingite-arsenopyrite thermometry yields a temperature range of about 560°–600°C while arsenopyrite compositions in the $f(\text{S}_2)$ -buffered assemblage (arsenopyrite+pyrite+pyrrhotite) yields temperature range of 375°–390°C at $\log f(\text{S}_2) = -9.7$ to -7.5 (Sahoo 2012; Sahoo and Venkatesh 2013). Most of the pyrite grains and arsenopyrite grains are zoned and submicroscopic gold occur as inclusions along the zoned portions and cracks of the sulfides which indicate a later fluid activity and remobilization of gold during metamorphism. It is assumed that remobilization of gold took place during the metamorphism of carbonaceous material as evidenced from the concentration of nano-scale inclusions within the cracks that are developed within the zoned sulfides (figure 2e). The invisible gold concentration varies from 900 to 3600 ppm in arsenopyrite and 700 to 2300 ppm in pyrite (Sahoo and Venkatesh 2013).

6. Discussion and conclusions

Carbonaceous matter in pelitic rocks is sometimes a mixture of poorly crystallized organic matter and well-crystallized graphite detritus. At low metamorphic grades up to greenschist facies, the organic composition of the precursor material controls the process of graphitization (Diessel *et al.* 1978; Buseck and Bo-Jun Huang 1985). The graphitization of carbonaceous units may be accelerated in the presence of carbonates and carbonate veins that traverse the region containing calcite and ankerite (Sahoo 2012). The graphitization process of a carbonaceous unit is thus considered to be

controlled mainly by the temperature, interacting fluid, nature of the lithology and organic matter content of the lithology.

Detection of carbonaceous phases like methane, graphite, and CO_2 in inclusions by Raman analysis reveals that a highly reducing environment prevailed during the mineralization. The ubiquitous host carbonaceous litho-association with the gold mineralization in Kundarkocha gold mine may be explained by reactions that convert C from reduced graphitic host rocks into CO_2 and reduce ferric iron in the host rocks to ferrous iron in biotite and chlorite. Hence, both CO_2 and CH_4 produced by reaction of H_2O with graphite, effervesced under the lower confining pressures in the veins (Williams 2007). This would have partitioned H_2S into the vapour phase, destabilizing Au-bisulfide complexes (Mishra *et al.* 2001; Saha and Venkatesh 2002) and the loss of CO_2 and H_2S from the aqueous phase caused precipitation of gold (Venkatesh *et al.* 2004). Black shale-hosted ‘Orogenic gold’ deposits may have a similar multi-stage origin that commenced with syngenetic gold accumulation in black shales (Distler *et al.* 2004; Deol *et al.* 2012).

Micro-scale inclusions of gold within the arsenopyrite zoning and cracks of pyrite indicate remobilization of gold during metamorphism of carbonaceous rocks. Role of carbonaceous units in gold deposition as established from other gold deposits (Springer 1985; Bierlein *et al.* 2001; Craw 2002). Similarly, in Kundarkocha, the organic carbon also could have played some role in facilitating the required reducing environment. Total organic carbon content varies from 0.155 wt% in carbonaceous rocks to 1.219 wt% in graphite (table 1). The

Table 1. Total Carbon (TC) and Total Organic Carbon (TOC) values of the mineralized carbonaceous rocks from Kundarkocha.

Sample no.	TC (mg)	IC (mg)	TC (%)	IC (%)	TOC (%)
CS-1	20.8	20.3	2.7	1.5	1.2
CS-2	20.3	19.7	4.1	3.5	0.6
CS-3	20.2	20.2	6.2	6.0	0.3
GS-1	20.3	19.9	1.9	1.0	1.1
GS-2	20.5	20.5	1.1	0.0	1.2
GS-3	20.4	20.4	1.2	0.0	1.2
GS-4	20.2	20.8	1.4	0.2	1.2
GS-5	20.8	19.7	5.4	4.8	0.6
GS-6	20.3	20.4	3.8	2.3	1.5
GS-7	19.9	20.1	1.2	0.0	1.2

Index: CS: carbonaceous shale/phyllite/slate; GS: Graphitic Schist; TC: Total Carbon; IC: Inorganic Carbon; TOC: Total Organic Carbon.

carbon content in graphitic schist associated with gold mineralization at Kundarkocha is markedly lower and possibly signifies the partial maturation of the carbonaceous material during metamorphism (Landis 1971; Buseck and Bo-Jun Huang 1985). Mixing of CO₂-bearing water with CH₄ could have been the prime factor for deposition of graphite (after Craw 2002):

Gold deposition is aided by the fluid interactions (redox reactions) with organic/inorganic carbon from the carbonaceous rocks which may be explained using the following reactions (Neall and Phillips 1987):

The interaction of the sulfide-rich solution, carbonaceous rocks, and the sulfide enrichment can be described as (after Craw 2002):

Necessary reducing environment is created by the interaction of organic matter within the host carbonaceous units that facilitated precipitation of metals (Mastalerz *et al.* 2000). Strongly reduced carbonaceous host rocks could have paved the way for partial reduction of fluid possibly creating deposition mechanism for gold. FTIR spectra exhibit distinct peaks of kerogen and other organic functional groups (figure 4) which signify substantial organic activity in the formation of the Kundarkocha gold deposit. There is a marked amount of TOC content within the graphitic material which is part of the volcano-sedimentary rocks, suggesting the possible role of organic activity in the mineralized belts during Precambrian. Some of these phases probably represent metamorphic alteration/hydrothermally altered fragments of an amorphous type of kerogen. Regarding the genesis of graphite or graphitic schist, shearing and fluid flow might be the reason triggering graphitization of carbon along the small scale shear zones under metamorphic conditions (Bierlein *et al.* 2001). Due to the variable nature of precursor kerogen and its response to temperature and time, organic matter maturation is seen in carbonaceous phyllites and slates (Ahn *et al.* 1999).

Localized shear fractures act as primary focus for fluid flow, channeling CO₂-rich fluids generated by devolatilization reactions (Phillips and Powell 2010). The precipitation of carbonates in such alteration zones coincides with a marked decrease

in gold solubility (Phillips and Groves 1983). The presence of such fluids is therefore thought to be critical in the development of gold mineralization. Fluid-rock interactions may be the cause of phase separation that occurs in response to the generation of CH₄ during reaction between hydrothermal fluids and carbonaceous wall rocks (Gu *et al.* 2012). Overall, the system appears to have evolved from a carbonate dominated regime to an aqueous regime through time owing to the devolatilization reactions involving alteration of the immature carbonaceous units responsible for the gold mineralization (Venkatesh *et al.* 2004). The CH₄ is attributed to localized reactions between hydrothermal fluids and wall rocks/the proximal carbonaceous sources such as carbonaceous phyllites/shales/graphite (Bottrel *et al.* 1988).

Gold deposition may result from fluid mixing between deeply sourced CO₂-bearing fluids and locally derived, more reduced methane bearing fluids. This implies that the CH₄ is a product derived from fluid-wall rock interactions (Gu *et al.* 2012). The spectrum of fluid compositions exhibited by the fluid inclusions also strongly supports fluid mixing as one factor influencing the composition of fluids and thereby transporting and precipitating Au. The mineralization is associated with carbonaceous material (containing organic carbon) in the form of a graphitic zone within the interface between the carbonaceous phyllite/black shale and chlorite schist. This may be considered as a marker zone or indicator zone for mineralization in Kundarkocha gold deposit and may provide definite clues for the exploration of gold in the analogous areas as a regional guide, which has been hitherto unrecognized so far.

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