Invisible gold in the high-sulphur Tertiary coals of Northeast India

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During an investigation of some high-sulphur coals from Meghalaya, Northeast India, with respect to their trace metal content, we recorded the occurrence of gold in iron sulphides (pyrites/marcasite) associated with such coals. A maximum of 6 mg/l gold has been recorded in the pyrite concentrates. Gold is lattice-bound and occurs in 'elemental form', forming solid solutions within iron sulphides. It is inferred that the iron sulphides are mostly syngenetic with coal and gold is concentrated in iron pyrites by biological activity during their precipitation and by inorganic adsorption process during recrystallization in a reducing environment.

Keywords: Gold, sulphur, tertiary coal, trace metal.

THE study of trace elements in coal has gained importance worldwide because of two reasons: one to assess the HAPs (hazardous air pollutants)[1], and the other to assess the presence of high-value elements or metals such as gallium and germanium that may prove beneficial, if they are present in significant quantities[2,3]. However, this type of study is rather limited in India. Though some work has been done by the Geological Survey of India[4,5] and the Central Institute of Mining and Fuel Research (erstwhile CFRI), Dhanbad[6], occurrence of noble metals, especially gold has not been reported from Indian coals. The Clarke value (or the average value of a chemical element in the earth's crust) for gold is not well constrained[7], but is considered to be around 0.005 ppm. There are not many data available on the accumulation of gold in coal. Gold content up to 17 ppm was reported in ashes of Cambria coal in northeastern Wyoming[8]. According to Goldschmidt and Peters[9], the concentration of gold in coal ash ranges from 0.02 to 0.05 ppm. In Czechoslovakia, Koblic[10] reported 35 ppm of gold from anthracite, and Bouška[11] reported trace amounts of gold in ash from the Anežka seam in the Sokolov Basin. Sheibley[12] mentioned about 0.15 ppm gold in coal ashes as an average. Chyi[13] reported the distribution of gold in coals of western Kentucky that were in ppb levels. In most of these reports, the mode of occurrence of gold has not been confirmed or discussed. Gayer and Rickard[14] reported the occurrence of gold in coals of New South Wales and claimed it to be the 'first record of native gold in coal'. Subsequently, two short notes were published in the *Journal of the Geological Society of India*[15,16], making appeals to investigate the Indian coals in respect of noble and platinum group of metals, citing the articles published in *Nature*[14] and *Economic Geology*[17]. However, to our knowledge, there is no published literature on the occurrence of gold in any of the Indian coals. In this communication, we report the presence of gold in high-sulphur coals of Northeast India. The mode of occurrence and genesis of gold have also been discussed.

Bulk samples (about 50 kg each) of coal were collected from four different sources in Meghalaya. Three pyrite-rich, hand-picked samples were also collected that contained pyrites of even more than 4 cm (in larger dimension) in size. For some strategic reasons the exact localities of sample collection are not disclosed here. The head samples were drawn from all the four bulk samples after crushing to –6 mm and following the conventional coning–quartering method. Four size fractions (–6 + 1.65 mm, –1.65 + 0.42 mm, –0.42 + 0.15 mm and –0.15 mm) were prepared using the standard Tyler-series screens and five density fractions (<1.4, 1.4–1.6, 1.6–1.8, 1.8–2.0 and >2.0) were generated from each size fraction using heavy liquids of different specific gravities (using bromoform and benzene). All the size and density fractions were studied under a Leica zoom stereo-microscope. It was found that pyrites were fairly liberated in size fractions below 0.42 mm and most pyrites were liberated below 0.15 mm. Pyrites were concentrated in finer size fractions with densities more than 1.8 and 2.0. Subsequently, each density fraction was analysed for its sulphur and some trace metal contents, including gold. In some samples pyrite concentrates were also generated using a mineral separator. Proximate analysis was done using a coal analyser (Anamed make; model 490), where fixed carbon was calculated by difference. On a moisture-free basis, the head samples analysed volatile matter: 36.1–38.9%; Ash: 14.5–23.0%, and fixed carbon: 39.5–47.6%. Sulphur contents were determined according to the standard procedure mentioned in ASTM D 2361–95. For trace metal analysis (including gold), a representative sample of coal was ashed at 525°C. The ash was then fused with lithium metaborate ($LiBO_3$). The melt was dissolved in dilute hy-

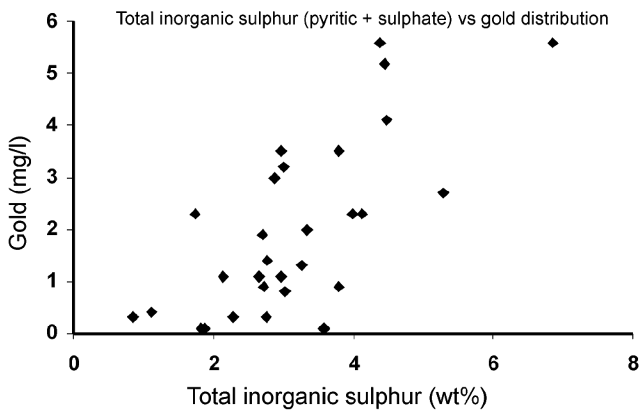

Figure 1. Total inorganic sulphur content (in wt%) of various pyrite-rich fractions vs their gold content (in mg/l) that shows a positive correlation.

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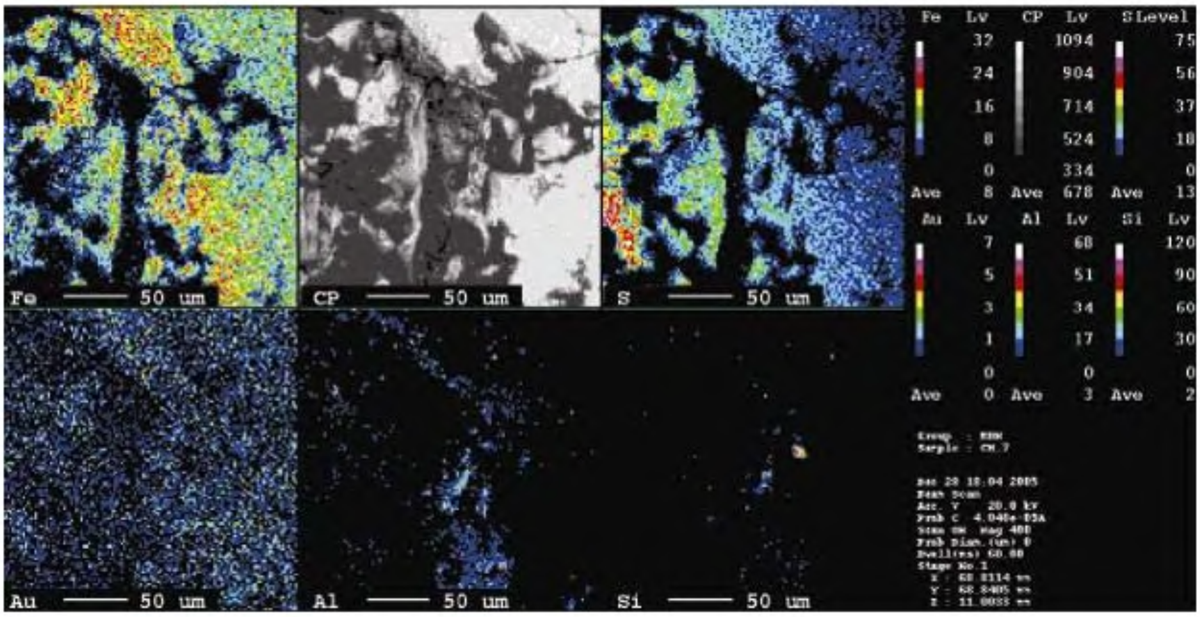

Figure 2. Backscattered electron image (CP, top central photo) of coal (grey-black) containing pyrite (whitish) and the corresponding X-ray image maps for Fe, S, Au, Al and Si revealing the association of gold with pyrite. Sample studied under EPMA (JEOL Superprobe JXA-8100).

drochloric acid (HCl) and the resultant solution analysed by inductively-coupled plasma optical emission spectrometer (ICPOES, Liberty Series II, Varian-make). Gold was not detected in any of the head coal samples. However, almost all the finer fractions (<0.42 mm) with higher specific gravities (>1.8) were analysed for gold. In few fractions gold content close to 6 mg/l was recorded. All these fractions were rich in pyrite. Therefore, it was inferred that gold may be associated with these pyrites. A plot between the gold-bearing fractions and the inorganic sulphur content of these samples (Figure 1) clearly shows a positive correlation, indicating the association of gold with iron sulphide.

X-ray diffraction studies (using Seifert XRD 3003 PTS with Co-target and Siemens D-500 with Cu-target) of some pyrite concentrates revealed the presence of marcasite and quartz in addition to pyrite. Polished sections were prepared from pyrite pieces separated out of pyrite-rich, hand-pick samples and the pyrite concentrates. These sections were studied under reflected light using a Leitz (Leica) orthoplan optical microscope. Only pyrite and marcasite were recognized. The presence of gold in any form could not be confirmed. Therefore, the same sections were studied under EPMA (electron probe micro-analysis) at the Institute of Minerals and Materials Technology (erstwhile RRL), Bhubaneswar using a JEOL Superprobe JXA-8100 and at the Indian Bureau of Mines, Nagpur using Cameca SX-100. The presence of gold as an independent phase could not be confirmed in any of these sections. However, X-ray image maps of pyrites revealed the presence of gold in these iron sulphides. After scanning a number of grains, it was confirmed that gold is present in 'elemental form' bounded in the lattice of these pyrites (Figures 2 and 3). Various forms of pyrite such as framboidal, colloform, recrystallized, discrete grains, bedded, massive and dendritic have been recognized in these coals[18]. It appears that most pyrites originally precipitated from iron-rich sols/gels as colloform bands or as framboids (Figure 4). Subsequently, the other forms of pyrite were developed due to recrystallization.

Although pyrite occurs in various forms, mostly it is syngenetic with coal. Singh and Singh[19] have also interpreted a syngenetic origin for these pyrites. Other modes of occurrence as veins, cavity-, fracture- or cleat-fillings, though supergene in nature, are locally confined within the coal. Therefore, pyrites acquiring gold from some hydrothermal (or igneous) sources is ruled out. Also the arsenic content of the pyrites is insignificant and erratic in nature. Transportation of gold by groundwater is highly unlikely as there is no known gold deposit in the region. In all probability, we interpret that the original source of gold is the coaly matter itself. The accumulation of gold in plants is not unnatural and has been reported from horse-tail ashes. Traces of gold have also been identified in the ash of beeches, hornbeams and other trees. For example, Němec *et al.*[20] found 0.062% gold in the ash of *Equisetum palustre* and 0.0063% gold in *Equisetum arvense*. Gold content of 0.11% was recorded from *Clematis vitalba* and traces of gold from *Salix capna*[21]. Data on gold content in other plants are also reported[22–24].

Therefore, we conclude that gold has been acquired/adsorbed by pyrites during their precipitation as framboids or colloform bands and subsequent recrystallization/growth. Pyrite framboids are mostly interpreted as biogenic, i.e. fossilization of bacterial colonies[25,26]. Figure 4 clearly reflects bacterial activity in precipitating

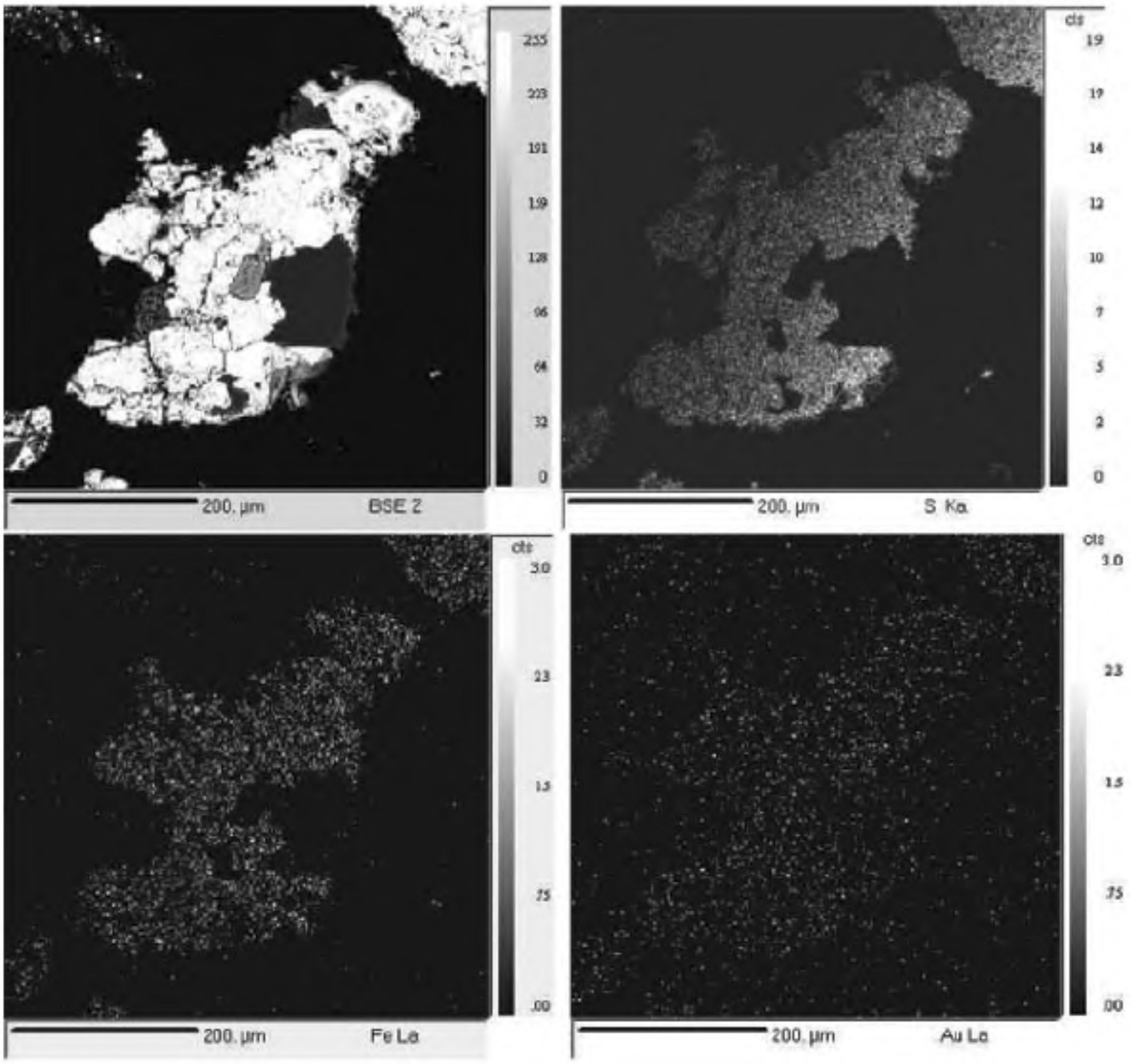

Figure 3. Backscattered electron image of a liberated pyrite grain (whitish) and the corresponding X-ray image maps for S, Fe and Au, showing the association of gold with pyrite. Sample studied under EPMA (Cameca SX-100).

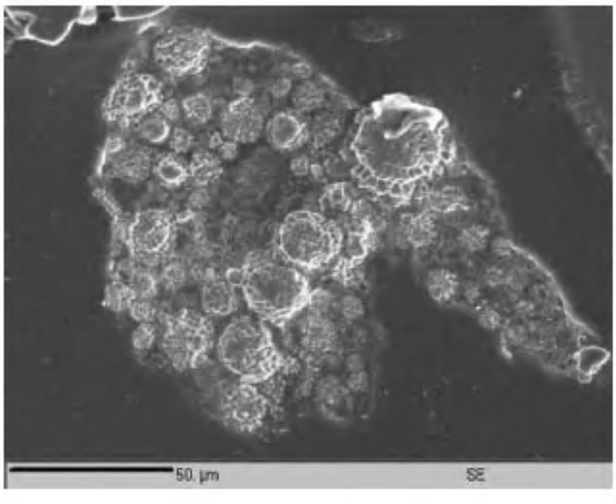

Figure 4. Secondary electron (SE) image of framboidal pyrite in coal from Meghalaya showing honeycomb structure (manifestation of biogenic activity of bacteria). Sample studied under EPMA (Cameca SX-100).

pyrite in the area. The bacterial colonies comprising sulphate-reducing bacteria might have acted as a site of high sulphide production and consequent precipitation of iron sulphide. The colloform pyrite may have formed diagenetically from iron-bearing gels. During both the processes (viz. biological and inorganic recrystallization) gold has been captured from the coaly matter and adsorbed into the structure of iron di-sulphides. Selective adsorption of gold into pyrite has depleted the gold content in the carbonaceous organic portion of coal in the high-sulphur Tertiary coals of Northeast India.

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Scorpion sting: A study of the clinical manifestations and treatment regimes

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Envenoming by an Indian red scorpion causes severe cardiovascular manifestations due to autonomic storm. Alpha-1 receptors stimulation plays an important role in the pathogenesis of acute refractory pulmonary oedema due to scorpion sting. Prazosin is a pharmacological and physiological antidote to scorpion venom actions. Since the advent of prazosin, the fatality is reduced to <4%. The time between the sting and administration of the first dose of prazosin for symptoms of autonomic storm determines the outcome, making this cheap drug a life-saving medicine. Early administration of scorpion antivenin within 1–2 h with oral prazosin enhances the recovery. Prazosin is a simple, cheap and easily available antidote which can be administered at primary health centers and free from anaphylaxis.

Keywords: Autonomic storm, dobutamine, prazosin, scorpion, sodium nitroprusside.

SCORPIONS (order Scorpionida) are the most venomous arachnids inflicting an extremely painful sting, although all are not fatal to human beings. The phylogenic origin of scorpions is not exactly known, although it is presumed that they have evolved from the extinct Eurypterids – the giant aquatic scorpions that lived during the Silurian period. The most striking feature of the scorpions are the large-sized pedipalps, which are furnished with stout chelae and the division of the abdomen into two segments; the post-abdomen segment is a slender, tail-like division or cauda, at the end of which is the large poison sting which camouflages itself as an additional segment. All scorpions are strictly nocturnal in habit. They are considered to be shy and sting when encountered in their hideouts such as burrows beneath boulders, bricks, barks and crevices of logs and trees. Although all three categories of scorpions, viz. burrowing (pelophilous), rock-dwelling (lithophilous) and arboreal are found in India, there is a general paucity of information in the country on the ecology of scorpions[1].

This communication focuses on *Mesobuthus tamulus* (MT; Indian red scorpion) and *Palmoneus gravimanus* (black scorpion), two of the most common scorpion species of India. Of the two, MT is the most lethal among all poisonous species of scorpion[2], while the black scorpion is less lethal and causes only severe local pain without systemic involvement[3]. Scorpion venom is a potent sodium channel activator[4] and envenoming by MT results in sudden pouring of endogenous catecholamines into circulation due to the autonomic storm evoked by delayed

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