# Mineralogical and Electron Microprobe Studies on the Cobalt Sample From Kalyadi Copper Deposit, Hassan District, Karnataka

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#### Abstract

The copper-cobalt deposit from Kalyadi, Hassan district is located between Sigegudda and Nuggihalli greenstone belts of Karnataka Craton. The cobalt mineralisation is mostly in banded, cherty and feldspathoid quartzite. The cobalt sample under investigation has been characterized by a variety of techniques including electron microprobe studies. The microprobe studies on sulphide grains were done to study the chemistry and elemental replacement in their lattice structure. The cobalt is present up to 3.21 wt% in pyrite grains whereas it is not present in chalcopyrite and arsenopyrite. Cobalt has preferably replaced iron in pyrite, which is of volcanic - exhalative origin.

### INTRODUCTION

Cobalt is considered to be a strategic metal, owing to its extensive use in aviation and defence industries. The conditional Indian resources of ore as per UNFC are estimated at 44.91 million tonnes (IMYB, 2004). It is estimated that the demand of cobalt in an optimistic scenario could be about 63700 tonnes by 2012 (Searle, 1998). There is no primary production of cobalt in the country. The demand of cobalt is mainly met through imports in the form of cobalt and cobalt base alloys, waste and scrap of cobalt and cobalt matte etc. The Kalyadi copper mine situated in Hassan district of Karnataka, India, is estimated to contain a reserve of about 5.8 m tonnes of cobalt ore and assays 400 - 600 ppm (Parameswaraiah, 1996 and Krishna Rao, 1998). The cobalt is present in pyrite, which constitutes 4-5% of the ore. The Kalyadi deposit was worked primarily for recovering the copper values by flotation of chalcopyrite in a plant of 200 - tpd capacity, while tailing constituting the bulk of cobalt was impounded in a tailing dump.

### GEOLOGY

The copper-cobalt deposit from Kalyadi, Arasikkere Taluk, Hassan district is located between Sigegudda and Nuggihalli greenstone belts of Karnataka Craton. It is geographically near to the Eastern limb of Holenarsipur schist belt. The area represents remnants of the oldest volcanic and sedimentary rocks fragmented and engulfed by later gneisses. The mineralisation is mostly in banded, cherty and feldspathiod quartzite.

In Kalyadi, the copper-cobalt mineralisation is found in metamorphosed and deformed volcanosedimentary formations located amidst peninsular gneiss (Fig.1). The Peninsular gneissic complex consisting mostly of banded and foliated granite - gneiss carrying lensoid bodies of leucocratic, medium to coarse grained and occasionally porphyritic granite and foliated biotite gneiss covers a major part of the area. The Dharwar schist band at Kalyadi consists of long narrow lensoid bodies of metavolcanic and metasedimentary suite of rocks occurring within the peninsular gneiss.

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The rock types in the area consists of amphibolite, banded ferruginous quartzite, chlorite- actinolite schist, quartz- biotite – chlorite - schist and quartzite. Dolerite dyke intrudes the schistose rocks.



Fig. 1: Geological Location Map of Kalyadi Area

# MATERIALS AND METHODS

### Sample Characterization

Mineralogical studies were done on the samples collected from the ore body. The instrumental studies were done on the sulphides concentrated by flotation techniques from the tailing dump to identify the cobalt phase.

Chemical analyses of the sample as a whole were carried out using standard wet chemical analysis technique.

# X-Ray Diffraction Analysis

X-ray diffraction analysis was carried out on a representative part of the sulphide concentrate, using model JDX -8030 X-ray powder diffractometer system, of JEOL Ltd, Tokyo, Japan.

### **Microprobe Analysis**

A representative part of the sulphide concentrate was drawn by coning and quartering method to prepare a polished mould, which was carbon coated in Boc Edwards Auto 306 carbon coating machine to suite the EPMA study requirements. Mineralogical charecterisation of the sample was carried out by CAMECA SX100 Electron Probe Micro Analyser (EPMA). Backscattered electron (BSE) imaging techniques, qualitative analyses and quantitative analyses are employed for the purpose using PEAK SIGHT on line software program. Care was taken to avoid the interferences between spectral lines of different elements of interest based on already tested in-house programs. The generated data was corrected by using an on line PAP- correction program.

## INSTRUMENTAL STUDIES

### Mineralogical Analaysis

The necessary polished and thin sections were made to study the different mineral constituents and textural features. The approximate percentages of the various mineral constituents present in the sample are summarized in Table 1.

Quartz is the predominant gangue mineral present with minor amounts of mica, carbonate, chlorite, apatite and magnetite. Among the sulphides, pyrite is the predominant opaque mineral present along with minor amounts of chalcopyrite, arsenopyrite and sphalerite.

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Mineral Constitution		Chemical Constitution	
Mineral	Percentage	Constituent	Assay %
Quartz	65-70	Co	0.032
Mica (biotite, muscovite)	7-10	Cu	0.096
Calcite	5-7	SiO <sub>2</sub>	75.85
Dolomite	4-5	Fe(T)	05.10
Pyrite	4-5	LOI	04.75
Chlorite	1-2	CaO	4.46
Amphibole	1-2	S(T)	1.85
Magnetite	1	MgO	1.82
Chalcopyrite	Traces	Al <sub>2</sub> O <sub>3</sub>	0.002
Apatite	Traces	P <sub>2</sub> O <sub>5</sub>	Traces
		Pb,Au,Ni,Ag	Traces

Anote at the destination of the second	<b>Table 1: Mineralogical</b>	and Chemical	Constitution in the	<b>Tailing Sample</b>
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# Quartz

Quartz is mostly fine grained and forms the matrix for the other minerals. At places, it occurs as aggregates of subhedral to anhedral (0.01 - 0.35 mm) size grains with well-sutured margins (Fig. 2). The medium sized quartz grains shows undulose extinction and are occasionally stretched and elongated showing lamination (Fig. 3). Fine-grained quartz is found intermixed with carbonate and chlorite. Quartz grains have undergone recrystallization leading to growth of grains.



Fig. 2: Quartz with Well Sutured Margins Crossed Nicols 100X)



Fig. 3: Quartz Stretched and Elongated

# Carbonates

Carbonates occur in minor amounts and are of two types - calcite and dolomite. They occasionally show rhombohedral cleavages and polysynthetic twinning. Carbonates occur as aggregates of irregular grains to isolated subhedral grains (Fig. 4). They are intimately associated and intermixed with fine-grained quartz.

# Mica

Muscovite and biotite mica occurs in minor amounts. They occur as books and flakes of 0.05 to 0.5mm size in association with quartz and chlorite.

# Chlorite

It occurs as 0.1 to 0.8 mm flakes and ropy aggregates within the fine grained quartz matrix. At places it is found along the lamination planes.

# Amphibole

Amphibole represented by actinolite is in very minor amounts and occurs as thin tabular prismatic

grains of 0.02 to 0.1mm in association with quartz and biotite. It often alters to chlorite, indicating retrograde metamorphism (Fig. 5).



Fig. 4: Isolated Grain of Carbonate



Fig. 5: Amphibole Altering to Chlorite

#### Pyrite

It is the main sulphide mineral present as coarse patches and fine disseminations.. Pyrite is fine to medium grained ( $60\mu$  to  $200\mu$ ). At places, coarse grains of pyrite (0.5mm to 1.5 mm) and perfect euhedra (Fig. 6) are also noticed. Pyrite of both metasedimentary and hydrothermal origin is noticed. The metasedimentry pyrite occurs as medium to coarse (0.6 to 5mm), anhedral to irregular grains with corroded margins. It is often, fractured and sheared. Hydrothermal pyrite occurs as independent medium size subhedral to euhedral grains with smooth margins and devoid of fractures (Fig 7). At places, it is elongated and broken (Fig.8). Occasionally it encloses medium sized chalcopyrite and quartz grains. It is often replaced by chalcopyrite along the grain boundaries and fracture planes (Fig .7). Pyrite is also noticed as fine disseminations in the silicate matrix (Fig. 9). Often, perfect porphyroblasts of pyrite (Fig 10) and mobilization of pyrite along the foliation (Fig 11) are also observed, which indicates the metamorphic features.



Fig. 6: Euhedra of Pyrite in Silicate (Reflected Light)



Fig. 8: Sulphides Broken and Elongated



Fig. 7: Pyrite with Smooth Margins. Note Chalocopyrite Replacing Pyrite. (Reflected Light)



Fig. 9: Fine Disseminations of Pyrite



Fig. 10: Porphyroblasts of Pyrite



Fig. 11: Mobilization of Pyrite

# Chalcopyrite

Chalcopyrite (Fig. 7) is present in minor amounts. Under the microscope, it appears brass yellow in colour with weak anisotropism. It occurs as fine to medium  $(20\mu \text{ to } 40\mu)$  size grains and also as veins and veinlets, irregular masses and anhedral grains in the silicate matrix. It generally replaces pyrite along the grain boundaries and fracture planes. It occasionally occurs as fine, randomly distributed, irregular droplets within silicate. At places, it encloses the euhedra of pyrite.

# Sphalerite

Sphalerite is found in trace amounts mostly in association with chalcopyrite. Under the microscope, it is grayish in colour and shows strain anisotropism. It is found mostly as subhedral medium grains of 0.04 - 0.15 mm in size

# Magnetite

It is present in very minor amounts. Under the microscope, it is grayish brown in colour and isotropic. It occurs as fine to medium (0.02 to 0.1mm) subhedral to euhedral grains randomly distributed in the silicate matrix.

Cobalt was not observed as a discrete mineral in the sample. So it may be present within the crystal lattice of pyrite.

# **Chemical Analysis**

The tailing sample and the sulphide concentrate were analysed for necessary radicals and the results are given in Table. 1 The sulphide concentrate assayed 1% cobalt.

# **X-Ray Diffraction Studies**

The X-ray diffractogram of the sulphide concentrate portrayed Pyrite as the major mineral followed by quartz (Fig 12). Trace amounts of chalcopyrite and sphalerite are also present. The results of the X-ray diffraction analysis are in good agreement with the mineralogical data.



Fig. 12: X-Ray Diffractogram of the Sulphide Concentrate

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#### **Microprobe Studies**

### Back Scattered Electron (BSE) Imaging

Extensive search of different fields by BSE imaging reveals that pyrite is the predominant mineral whereas chalcopyrite, arsenopyrite and silicate gangue are in very minor amounts. No other ore mineral could be identified. While chalcopyrite was found to be mostly free, arsenopyrite is mostly seen as inclusions within pyrite grains.

#### Qualitative Analyses

Qualitative analyses were carried out on various pyrite, chalcopyrite and arsenopyrite grains to find out which mineral amongst them hosts cobalt. The results (Fig 13) demonstrate that only pyrite in its lattice structure contains cobalt.



Fig. 13: Qualitative Analyses of Sulphides

#### Quantitative Analyses

Quantitative Analyses on various pyrite grains were carried out to estimate the amount of cobalt and other elements present in individual pyrite grain. The results are shown in Table. 2. The maximum cobalt content in the individual pyrite is found to be 3.21% and the minimum cobalt is 0.27%. Almost every analyzed pyrite grain contains as substituting element in the structure.

Sl. No:	S	Fe	Co	Total
1	53.19	43.79	3.21	100.19
2	53.49	43.82	2.87	100.18
3	53.15	44.41	1.72	99.28
4	52.53	45.90	0.78	99.21
5	52.89	45.93	0.72	99.54
6	53.31	44.80	2.04	100.15
7	52.62	45.07	1.97	99.66
8	52.43	44.59	2.84	99.86
9	53.73	46.23	0.27	100.23
10	53.78	45.66	0.92	100.36
11	52.99	45.15	1.57	99.71
12	52.92	45.13	1.80	99.85
Avg	53.09	45.04	1.73	99.85

Table 2: Quantitative Analyses of Individual Pyrite Grains (In Wt%)

### CONCLUSIONS

Mineralogical studies have indicated that quartz is the major mineral present with minor to trace amounts of mica, pyrite, calcite, chlorite, apatite, arsenopyrite, sphalerite, amphibole and chalcopyrite. No discrete cobalt mineral was noticed in the sample.

Chemical analysis data revealed that cobalt is present associated with pyrite.

Microprobe studies on different sulphides indicate that cobalt is present in the lattice structure of pyrite and not in chalcopyrite and arsenopyrite. Branov et al (1973) ascribes higher concentration of cobalt and other trace elements in pyrite either due to mechanical mixture or to elements isomorphously entering into the pyrite structure. According to Barnes (1979), higher concentration of cobalt over nickel in pyrite suggest, it is either sedimentary or hydrothermal origin.

The theoretical formula of pyrite is  $FeS_x$  (x < 2.0), which may be interpreted in two ways. First either as a structure with some sites vacant and secondly as Fe occupying some vacant S positions. Kullerud and Yoder (1959) suggested that within the limits of chemical analysis and cell measurements, pure pyrite has a sulphur to metal ratio of 2.00 : 1.00. Minor amounts of elements are often reported in pyrite. In a pyrite – chalcopyrite association, cobalt is preferably concentrated in pyrite. It is possible that these elements may be present in pyrite as solid solution substituting for iron.

The theoretical composition of pyrite is: Fe = 46.6 and S = 53.4. But, it can be seen from the microprobe analysis of the present investigation that Fe ranges from 43.79 to 46.23, which is less than the theoretical composition. In addition, cobalt concentration in different grains varies from 0.27 to 3.21. It can also be seen that when cobalt concentration is high, correspondingly Fe is less. It clearly shows that cobalt has replaced Fe.

Krisna Rao *et al* (1984) suggested a volcanic - exhalative origin for the ore body of Kalyadi deposit. The microprobe analysis carried out on chalcopyrite and arsenopyrite does not show any cobalt enrichment. This can be reasoned as paragenetically pyrite forms first followed by arsenopyrite and chalcopyrite. The cobalt might have entered in the first formed pyrite and by the time it crystallized, there might not have been any cobalt left to enter in chalcopyrite and arsenopyrite structure.

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