

# TRACE ELEMENTS STUDY BY ELECTRON PROBE METHOD IN SULPHIDES FROM KOLIHAN, RAJASTHAN, INDIA

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THE copper ore from Kolihan, Rajasthan, India, consists essentially of pyrrhotite and chalcopyrite with minor amounts of cubanite, mackinawite, pyrite, marcasite, magnetite, ilmenite, valleriite, arsenopyrite, ramalsbergite, sphalerite, tetrahedrite. Deb and Mukherjee<sup>2</sup> (1969) have studied mackinawite in detail and Rao and Rao<sup>6</sup> (1968) have given a detailed account of copper ore and associated sulphides.

The present paper deals with the trace element studies on sulphides from Kolihan section of Khetri copper project. Quantitative estimations of minor elements in pyrite, pyrrhotite, cubanite (orthorhombic, cubic), chalcopyrite, valleriite and mackinawite were made by Electron Probe Micro-analyser AEI model SEM<sub>2</sub>. Determinations of the elemental contents of the mineral were done at 20 Kv and the procedure incorporates corrections for instrumental drift and background counts and following the procedure of Springer<sup>7</sup> (1967) and Desborough<sup>3</sup> *et al.* (1968). The determinations are given in Table I.

## Distribution of Trace Elements

**Copper.**—The presence of copper is noticed in all sulphides in varying amounts. In pyrite and pyrrhotite the copper content is by 0.067 and 0.05% respectively. In one of the mackinawites the copper content is 5.35% (cuprian mackinawite) and in another mackinawite it is 3.15% (nickeliferous mackinawite Ni—6.3%).

**Nickel.**—Nickel in pyrite is 0.074% and in copper minerals it varies from 0.04 to 0.05%. In pyrrhotite it is up to 0.21%. Nickel in mackinawite varies from 0.1 to 0.195% and in one case it is up to 6.3%. The nickeliferous mackinawite is seen associated with cubanite and pyrrhotite occurring in mineralised amphibolite.

**Cobalt.**—Cobalt in pyrite is up to 0.096% and pyrrhotite contains 0.53%. Cobalt content in copper minerals is fairly constant; in mackinawite it ranges from 0.125 to 0.266% and in nickeliferous mackinawite it comes up to 0.45%. Kouvo<sup>5</sup> (1963) reports 0.2% cobalt and about 5% nickel content in Outokumpu mackinawites.

TABLE I  
Showing the chemical composition and minor elements in sulphides of copper ore from  
Khetri copper project (Average of 5 Scans)

Mineral	Composition	Copper%	Iron %	Sulphur%	Nickel %	Cobalt%	Manga- nese ppm	Vana- dium ppm	Lead ppm	Zinc ppm
Pyrite	FeS <sub>2</sub>	0.067	46.49	53.33	0.074	0.096	700	D.L.	50	200
Pyrrhotite	Fe <sub>1+x</sub> S	0.05	46.30	53.00	0.21	0.53	550	300	50	200
Chalcopyrite	CuFeS <sub>2</sub>	34.58	30.46	34.93	0.042	0.044	500	200	50	550
Cubanite	CuFe <sub>2</sub> S <sub>3</sub>	23.40	40.99	35.81	0.041	0.043	500	200	50	550
(Isometric)										
Cubanite	CeFe <sub>2</sub> S <sub>3</sub>	23.51	41.1	35.42	0.050	0.063	450	250	50	350
(Orthorhombic)										
Valleriite	Cu <sub>3</sub> Fe <sub>4</sub> S <sub>7</sub>	29.82	35.01	35.11	0.045	0.040	400	250	50	550
Mackinawite	FeS	0.05	60.3	39.4	0.147	0.137	550	D.L.	50	200
Mackinawite	FeS	0.05	61.4	38.3	0.129	0.125	500	D.L.	50	225
Mackinawite	FeS	0.05	62.5	36.8	0.133	0.266	550	D.L.	50	200
Mackinawite	FeS	0.05	63.2	36.4	0.106	0.233	600	D.L.	50	250
Mackinawite	FeS	0.05	64.8	34.9	0.107	0.155	500	D.L.	50	225
Mackinawite	(CuFe) <sub>1+x</sub> S	5.35	59.25	35.10	0.195	0.160	450	D.L.	50	300
(Cuprian)										
Mackinawite	(NiFe) <sub>1+x</sub> S	3.15	54.80	35.30	6.30	0.450	500	D.L.	50	300
(Nickeliferous)										
Mackinawite										
by O Kouvo	FeS	..	60.2±2	..	5.0±0.3	0.2	..	..	..	..
<i>et al.</i> ,	FeS	0.5	55.1±2	..	5.4±0.3	0.2	..	..	..	..
Outokumpu	FeS	0.5	53.1±2	..	5.4±0.3	0.2	..	..	..	..
ore in chalcopy- rite, cubanite										

D.L. = Detection limits.

**Manganese.**—Manganese is constantly uniform in all sulphide minerals ranging from 400 ppm to 550 ppm, and in pyrite it is 700 ppm.

**Vanadium.**—Vanadium is in less than detectable quantities in pyrite and mackinawite. In pyrrhotite, chalcopyrite, cubanite and valleriite it varies from 200 to 300 ppm.

**Lead.**—Lead content is uniformly about 50 ppm in pyrite, pyrrhotite and copper sulphides, and less than 50 ppm in mackinawites.

**Zinc.**—Copper minerals contain fairly high quantities of zinc ranging from 350 to 550 ppm, and in iron sulphides between 200 to 300 ppm.

#### DISCUSSION

The presence of nickel and cobalt in pyrite pyrrhotite and mackinawite samples is in conformity with the observations of earlier workers summarised by Fleischer<sup>1</sup> (1955) and Clark<sup>1</sup> (1970). In fact, nickel and cobalt could be expected to appear even in larger amounts, more so in mackinawite. Nickel and cobalt content is much variable in mackinawites collected from different rock types namely granetiferous chlorite schist (Co—250 ppm, Ni—580 ppm, Cu—2000 ppm), amphibolites meta-dolerites, mafics, etc. (Co—2750 ppm, Ni—230 ppm, Cu—2000 ppm) mineralised zones (Co—120 to 850 ppm, Ni—125 to 1250 ppm, Cu—2000 ppm) thus bearing a genetic significance of the ore bodies to rock types.

Copper amongst the chalcophile elements is consistently present in all the iron sulphides and to the tune of 3 to 5% in the mackinawites forming a phase in the part of the system Cu-Fe-S or as a member of an extensive cuprian mackinawite solid solution series [*i.e.* (Cu, Fe)<sub>11+2</sub>S].

Lead is relatively in smaller quantities than zinc and both of them become relatively enriched in

the later stages forming sphalerite and lead presumably in solid solution with later sulphides since it is not seen as separate mineral.

Vanadium and manganese are strongly oxyphile in nature and manganese can probably enter iron sulphides structure to a limited extent because of their close geochemical affinity. Vanadium is less than in detectable limits in pyrite and mackinawite.

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