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SHORT COMMUNICATIONS

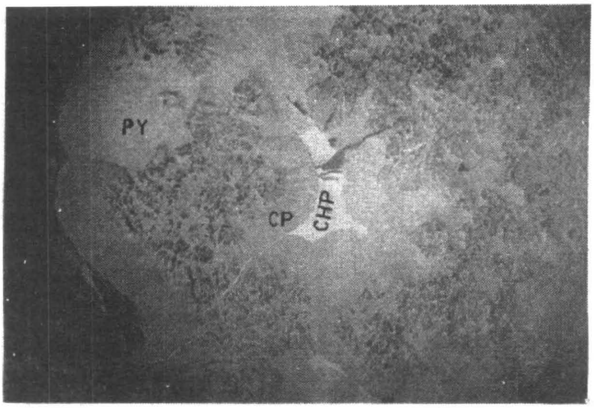
Occurrence of Copper Bearing Chalcophanite from Gottivada Manganese Ores, Eastern Ghats, Andhra Pradesh

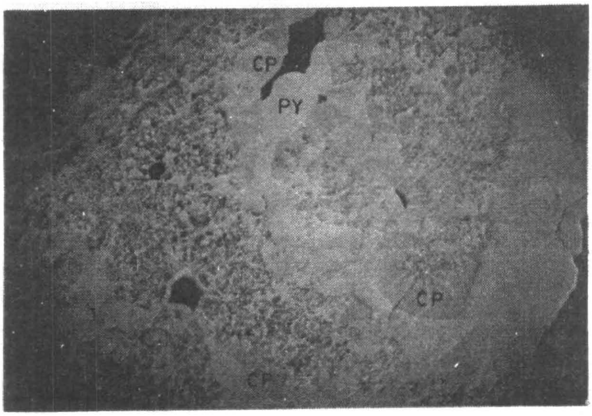
Chalcophanite (Zn, Cu) Mn_3O_7. $3H_2O$ is reported from Gottivada Manganese Ores (17°32'0"N - 82°44'50"E). The mineral crystallises in the triclinic system with a=7.5201, b=7.5102, c=8.1324 Å; α=90°, β=116°40', γ=120° space group P1. The structure of chalcophanite is characterised by single sheets of water molecules grouped in open double hexagon rings alternating with double oxygen layers. The seventh octahedral site in the structure is occupied by Mn, Zn and Cu atoms linked to the triads of oxygens. Bonding of the vacanies in the Mn layer complete the octahedral co-ordination with the triads of water molecules. Physical, optical and chemical properties of copper bearing chalcophanite are described in detail. The chalcophanite is a secondary colloform manganese mineral formed from the gels that contains copper and zinc atoms with manganese hydrolizates.

Introduction : During the study of Mn-minerals from Gottivada, the authors identified chalcophanite for the first time from the Indian Manganese Ore deposits. Crystal structure of chalcophanite was described earlier by Wadsley (1955), Radtke *et al.* (1967) with the chemical composition Zn Mn_3O_7. $3H_2O$. Ostwald (1981) recorded that chalcophanite formed as a result of a low temperature topotactic transformation from the clay. The chalcophanite crystals are in the form of radiating aggregates of thin lamellae (Figs.1, 2 and 3) encrusting and in association with cryptomelane, pyrolusite, chalcopyrite, pyrite, franklinite and graphite. The mineral shows a characteristic pale brownish grey colour in reflected light with distinct bireflectance in shades of creamy whitish grey. Chalcophanite is readily cleaved parallel to (001). It is anisotropic and shows brownish red internal reflections. Reflectance at 546nm in air is 21.22% and VHN at 100 g load is 220.

Methods of Study: Optically pure mineral separates were carbon coated and subjected to Wavelength Dispersive Spectrophotometer-X-ray counting system (WDS-SRCS) attached to Scanning Electron Microscope (SEM) (Fig.3c) (JOEL JSM-T 330A) using acceleration potentials of 20 KV and Perkin Elmer Atomic Absorption Spectrophotometer (AAS) for chemical analysis. International standards [FeR_2, FeR_4 (G.S. Canada), GTI-IW of France and G_2 of USGS] were used during analyses with the instruments WDS/SEM and AAS. Optically pure, diamond scrapped mineral grains were subjected to X-ray diffraction on Phillips X-ray diffraction system PW 1730/PW 1390 (Cu-Kα radiation) and the data given in Table I. The dÅ values at 6.9642, 4.0800, 3,500, 3.3300 and 2.2544 exhibited in the XRD are almost similar to that of chalcophanite described by Wadsley (1955) and data provided in JCP DS file data No.15-807.

From the X-ray data, it is clear that chalcophanite has a layered structure with a sequence- Mn-O-Zn-H_2O-Cu-O-Mn-O and forms infinite two dimensional sheets. Every seventh metal site is vacant causing a trigonal grouping of empty octahedral sites at a parting





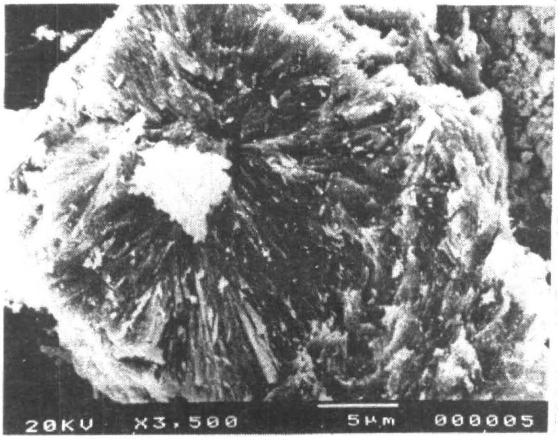


Fig.1. Microphotograph showing chalcophanite (CP) radiated laths enclosed in pyrolusite (Py) and bordered with chalcopyrite (CHP) (under reflected light - 40X).

Fig.2. Microphotograph showing chalcophanite (CP) Microfine radiated laths enclosed in Pyrolusite (Py) and Manganese Wad. (under reflected light 80X).

Fig.3. Scanning Electron Microphotograph showing radial laths of chalcophanite.

Table I X-ray data on chalcophanite

dÅ	I_0/i_1	(hkl)	Crystallographic Constants		
6.9642	100	001	Crystal System	=	Triclinic
6.2300	20	010	a_0	=	7.5201
4.0800	50	011	b_0	=	7.5102
3.5000	60	112	c_0	=	8.1324
3.3300	60	121	α	=	90°
2.5700	40	021	β	=	116°40'
2.4565	30	130	γ	=	120°
2.4501	40	113	Space groupP1		
2.3008	35	231	Z	=	2
2.2544	50	213	D_X	=	3.81
1.8468	20	031	D	=	3.76
1.7951	10	233	D_X	=	Density Calculate fromx-ray data
			D	=	Density measured

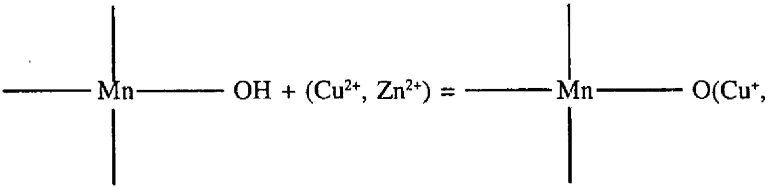
Table II Chemical analysis, structural formulae of chalcophanite from Gottivada

	Wt % WDS/SEM Method	Wt % AAS Method
MnO	72.96	72.94
CuO	4.81	4.80
ZnO	2.29	2.30
CaO	0.14	0.14
BaO	0.41	0.40
MgO	0.03	0.03
Na_2O	-	-
K_2O	0.82	0.81
P_2O_5	0.13	0.12
TiO_2	0.02	0.02
H_2O^+	10.06	10.04
H_2O^-	6.14	6.14
	97.81	97.74
	Structural formula on the basis of 7(0)	
n^{2+}	3.54	3.54
Cu^{2+}	0.21	0.20
Zn^{2+}	0.10	0.09
Ca^+	0.01	0.00
Ba^+	0.01	0.01
Mg^{2+}	0.00	0.00
Na^{2+}	-	-
K^+	0.06	0.05
P^+	0.00	0.03
Ti^+	0.00	0.0
	3.92	3.92

H_2O^+ determined by anhydrous sodium tungstate method
Mn is determined as MnO

distances of 7.5201 Å. Zn and Cu atoms are located above and below vacancies in the Mn layer by bond length of 1.92 Å to the oxygen atoms (Wadsley, 1955).

Discussion and Conclusions: The results of chemical analysis, recalculated on the basis of seven oxygen atoms are given in the Table II. During diagenesis Cu and Zn might have been released to form colloform sols and gels from chalcopyrite and franklinite which occur as embayed grain within the colloform bands. Sufficient quantum of Cu (0.210) atoms are available along with Zn (0.096) atoms in the sols. This Cu^{2+} has a value which, perhaps fortuitosly is in exactly excess value of Zn^{2+}. At higher pH values, MnO_2 sols was negatively charged and had a cation exchange capacity that increased with increasing pH as would be expected from an oxide whose surface charge is controlled by loss or gain of the protons. Adsorption of Cu^{2+} and Zn^{2+} was similar to that of Mn^{2+}. The adsorption mechanism is—



$$-\overset{|}{\underset{|}{\mathrm{Mn}}}-\mathrm{OH} + (\mathrm{Cu}^{2+}, \mathrm{Zn}^{2+}) = -\overset{|}{\underset{|}{\mathrm{Mn}}}-\mathrm{O}(\mathrm{Cu}^{+}, \mathrm{Zn}^{+}) + \mathrm{H}^{+}$$

Probably the uptake also involved phase transformations among the manganese oxides and catalysis of redox reactions by Mn^{2+}-Mn oxide system. As such, the reduced environment allowed copper into the structure of chalcophanite replacing Zn. X-ray powder diffraction studies also suggests that the Cu-materials are isostructural with Zn-bearing chalcophanite. hence, the authors propose the composition of Chalcophanite from the study are as (Zn, Cu) $Mn_3O_7.3H_2O$. Furthermore chalcophanite association with the low temperature manganese higher oxides like pyrolusite and cryptomelane in colloform bands suggests that the mineral is formed at low temperature supergene process as suggested by Ostwald (1981).

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References

Ostwald, J. (1981). Some observations on the mineralogy and genesis of chalcophanite. Miner. Mag, v.44, pp.109-111.

Radtke, A.S., Taylor, C.M. and Hewett, D.F. (1967). Aurorite, argentian Todorokite and Hydrous Silver Lead Manganese Oxide. Eco. Geol., v.62, pp.186-206.

Wadsley, A.D. (1955). The Crystal Structure of Chalcophanite $ZnMn_3O_7.3H_2O$. Acta. Cryst., v.8, pp.165-172.

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