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Lithiophorite and Chalcophanite as Secondary Mn-Oxides in Chromite Ores of Sukinda, Orissa, India

Minor amount of Mn oxides occur as veins and fracture fillings in some of the chromite ore samples of D-Quarry of South Kaliapani, Sukinda. Microscopic, XRD and EPMA studies indicate that the Mn oxide minerals are lithiophorite and chalcophanite. These minerals are enriched in Ni and Co and were formed by lateritic weathering of ultramafic rocks.

Introduction: The Sukinda chromite bearing nickeliferous ultramafic complex (21°-21°04': 85°40'-85°55') of eastern India has been investigated by many geologists for its immense geological and economic importance (Banerjee, 1972; Ziauddin *et al.* 1979). During the course of investigation on the characterisation and beneficiation of the low grade chromite ores of D-quarry of South Kaliapani mines (20°02' 30": 85°46'48") of Sukinda, some lumpy and semi-friable chromite ores were collected from a depth of about 10m from the surface of this newly opened up mine. The 40m wide chromite band is flanked on both hanging and footwall sides by thick nickeliferous limonite zones.

Microscopic Studies: Ore microscopic studies of some of the chromite ore samples reveal that little Mn oxides occur along the fractures and veins and as cavity fillings mostly in association with goethite. They occur as coarse to fine granular aggregates and radiating fibrous blades (Figs. 1, 2 and 3). At places the minerals occur in zones in which the fibrous crystals occupy the cores surrounded by the granular crystals (see Figs. 1 and 2). Micron sized granular crystallites replace chromite from grain boundaries and sometimes pseudomorphically retain the crystal outlines of the host. The granular phase of Mn-oxide is lithiophorite characterised by (a) coarse to fine polyhedral grains; (b) strong bireflectance from white to dark grey, bireflectance in air at 545 nm is between 8.9% to 18.8%; (c) VHN value at 25 gm load varies between 76 to 119 Newton averaging 102 Newton; (d) strong anisotropism with no internal reflection. The fibrous and acicular Mn oxide is chalcophanite characterised by (a) feathery and radiating form; (b) strong bireflectance from white to deep grey; reflectance in air at 545 nm is from 8.3% to 25.2%; (c) VHN value at 25 gm load ranges from 71 to 145 with average of 98 Newton; (d) strong anisotropism and no internal reflection even under oil. The presence of lithiophorite and chalcophanite in the chromite ore is confirmed by their characteristics d spacings (Fig. 4): Lithiophorite: 9.41Å, 4.67Å, 3.13Å; 2.34Å, 1.87Å, 1.56Å; Chalcophanite: 7.05Å, 2.56Å, 2.23Å, 1.59Å. The other minerals identified from XRD studies are chromite, goethite and hematite.

Chemistry: Electron probe microanalyses of lithiophorite and chalcophanite at several points in three aggregates in a chromite ore sample are given in Table I. The scan positions are shown in the Figs. 1, 2 and 3. The data reveal that (a) lithiophorite is aluminous (Al_2O_3 16.03%-24.99%) and contains high amount of NiO (7.69%-18.24%) and CoO (0.99%-3.42%); (b) chalcophanite contains lower amount of Co (max. CoO 0.99%) and Ni (max. NiO 12.45%) than the lithiophorite; it is also almost devoid of aluminum (max. Al_2O_3 0.78%) and Zn (max. ZnO 0.07%). Zinc deficient nickeliferous chalcophanite has also been described from the

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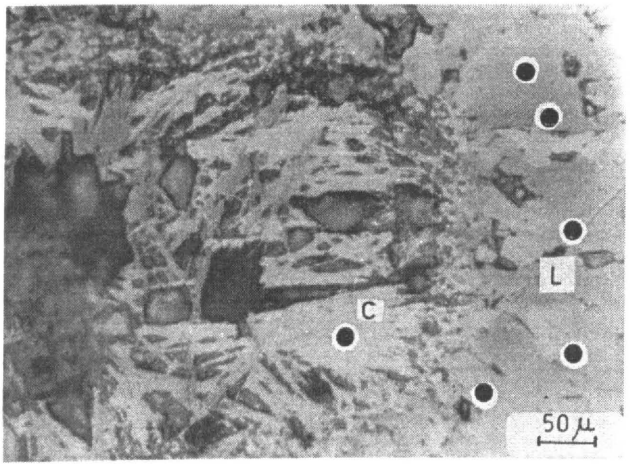

Fig.1. Coarse granular lithiophorite (L) (along the margin) and fibrous chalcophanite (C) (at the core) forming an aggregate (aggregate I). Reflected plane polarised light. ●- EPMA scan positions.

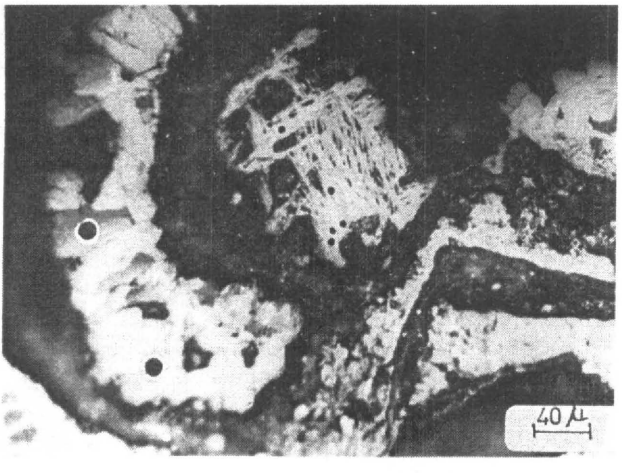

Fig.2. Granular lithiophorite and bladed chalcophanite occurring as cavity filling mass (aggregate II). Chalcophanite is partially mantled by lithiophorite. ●- EPMA scan positions.

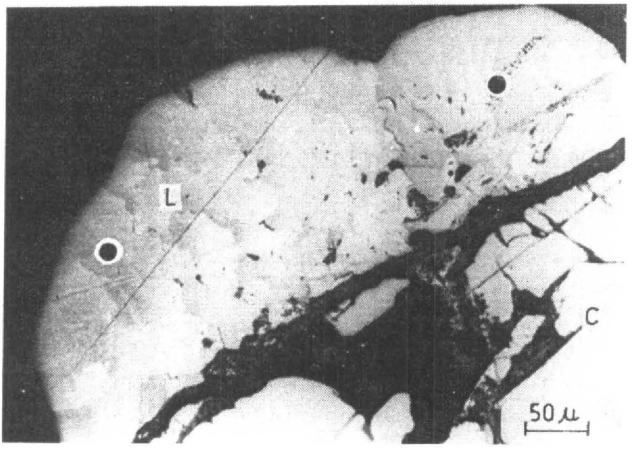

Fig.3. Granular lithiophorite (L) along a fracture. Chromite (C) is fractured. Aggregate III. ●-EPMA scan positions.

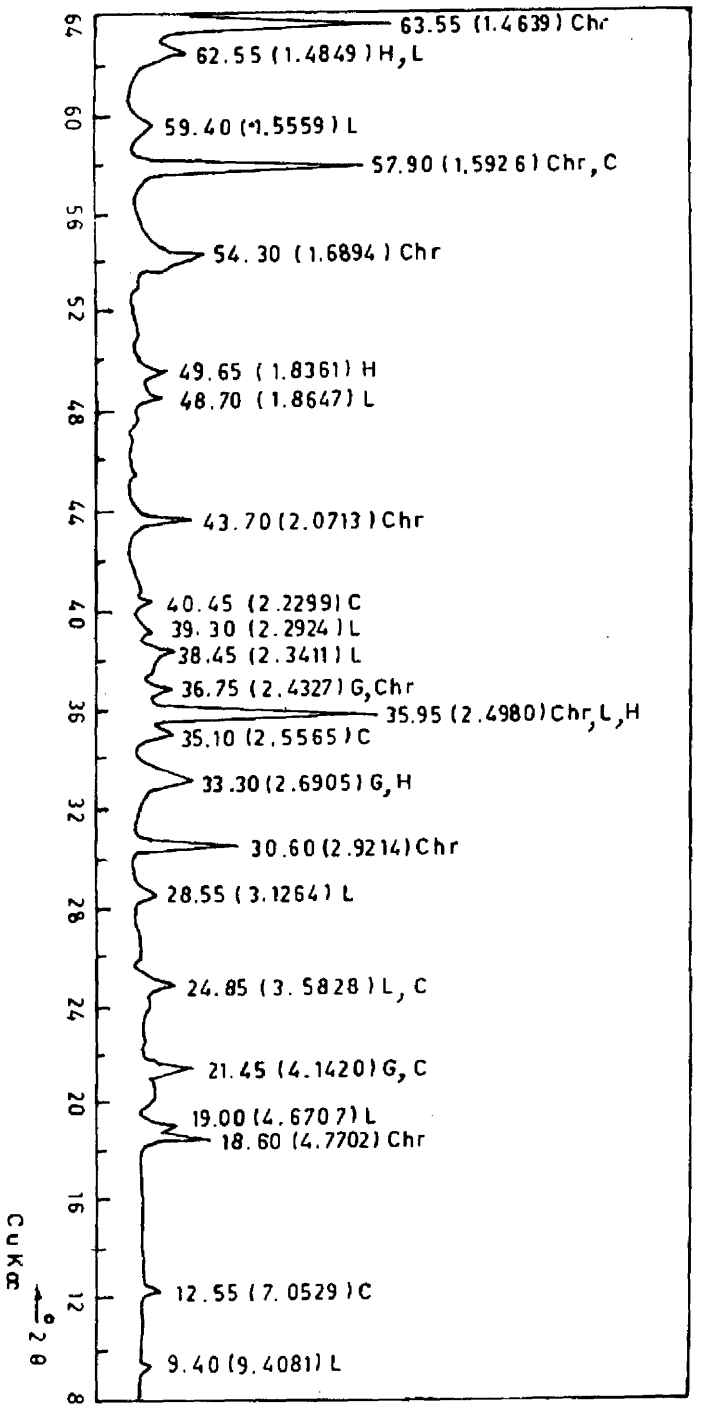

Fig.4. X-ray diffractograms (by Philips PW 1400 unit with Cu kα radiation) of a chromite ore showing the x-ray reflections of chromite (Chr), goethite (G), hematite (H), lithiophorite (L) and chalcophanite (C).

lateritic nickel cobalt deposits overlying ultramafic rocks of Kalgoorlie, Australia (Elias *et al.* 1981) (analysis no.6, Table I) and lateritic manganese deposits of Grooty Eyelandt, Australia (Ostwaldt, 1988).

Table I. EPMA analyses of lithiophorite and chalcophanite.

	Aggregate I			Aggregate II				Aggregate III		
Nos.	1		2	3		4		5		6
	Av.	Range		Av.	Range	Av.	Range	Av.	Range	
n	(5)		(1)	(2)		(5)		(2)		
MnO_2	46.15	45.18	58.86	48.16	47.70	66.46	64.21	48.82	49.33	61.35
		46.91			48.61		69.78		48.31	
Cr_2O_3	0.31	0.28	0.35	0.11	0.13	0.26	0.12	0.08	0.07	0.01
		0.39			0.08		0.27		0.08	
Fe_2O_3	2.34	1.91	0.68	1.33	1.14	0.39	0.17	3.16	2.35	0.18
		3.07			1.51		0.85		3.97	
MgO	0.41	0.27	1.58	0.80	0.61	1.85	1.69	0.18	0.14	0.61
		0.50			0.99		2.07		0.22	
Al_2O_3	20.10	19.39	0.78	16.03	16.03	0.04	0.00	24.22	23.44	0.19
		21.58			16.03		0.08		24.99	
TiO_2	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.08	0.03	0.01
		0.00			0.00		0.01		0.04	
CoO	1.93	1.32	0.99	1.07	0.99	0.75	0.62	2.59	1.75	1.78
		2.53			1.15		0.86		3.42	
NiO	11.14	10.78	9.03	16.29	14.34	12.16	11.73	9.08	7.69	11.61
		11.66			18.24		12.45		10.47	
V_2O_3	0.00	0.00	0.00	0.05	0.00	0.00	0.00	0.05	0.03	n.m.
		0.00			0.09		0.00		0.07	
ZnO	0.02	0.02	0.03	0.00	0.00	0.02	0.00	0.00	0.00	n.m.
		0.05			0.00		0.07		0.00	
Total	82.40		72.32	83.84		81.93		88.26		75.93
H_2O	17.60		17.68	16.16		18.07		11.74		24.07

Index: 1: Coarse granular lithiophorite along the boundary of aggregate I; 2: Radiating fibrous chalcophanite near the centre of aggregate I; 3: Granular lithiophorite of aggregate II; 4: Bladed crystals of chalcophanite at the core of aggregate II; 5: Lithiophorite in aggregate III; 6: Nickeliferous chalcophanite, Kalgoorlie, Western Australia (Elias *et al.* 1981). Data obtained by using an ARL SEMQ automated electron microprobe at the Institut fur mineralogie und lagerstattenlehre der RWTH, Aachen, Germany and corrected by the method of Bence and Albee (1968). n.m. - not mentioned; n- no. of point analyses. H_2O- By difference.

EPMA scan positions for aggregate I, aggregate II and aggregate III are shown in the Figs. 1,2 and 3 respectively.

Discussion: The Mn-oxide rich (wad, asbolane and/or lithiophorite, cryptomelane, chalcophanite etc.) horizons occurring as discrete masses, void and fracture fillings and discontinuous bands with high percentage of Ni and Co have been noted in many nickeliferous laterites overlying ultramafic rocks of the world (Golightly, 1981). In Sukinda ultramafic complex, Ziauddin *et al.* (1979) also reported occasional concretionary and irregular masses of Mn-oxides in the nickeliferous limonite ores which are formed by lateritic weathering of the dunite and serpentinite. The intensely fractured chromite ore bands provided suitable locii for chemical precipitation of manganese to form lithiophorite and chalcophanite under favourable Eh/pH conditions during weathering. The Mn oxides contain large amount of Co and Ni and it has been suggested that these elements can be introduced

both by coprecipitation and sorption into the pre-existing Mn oxide minerals (Kuehnel *et al.* 1978; Manaceau *et al.* 1978).

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