SHORT COMMUNICATION

Co-rich Lithiophorite in Manganese Ores of the Bonai-Keonjhar Belt, Orissa

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Abstract: Co-rich Lithiophorite is reported for the first time from low-grade Mn ores of the Bonai-Keonjhar belt (Jama-Korra valley), Orissa. It occurs in two distinct litho-host associations, (i) lateritic zone capping Mn-ore horizon and (ii) shear zone-controlled siliceous manganese ore. It mostly appears as thinly banded and as vug-filled linings, in close association with cryptomelane. It occurs as micron-sized accicular to pea-shaped crystallites in the first lithoassocation as coarse, radiating crystals showing zig-saw pattern arrangement in the second association. Co content is low (CoO 0.14-0.8%) in the fine-grained variety whereas in the coarse-grained variety it ranges up to 2% (CoO 0.14-2.00%). Appreciable quantity of Ni (NiO 0.15-1.5%) is observed along with Co only in coarse-grained variety. The mechanism of Co-entry into the two varieties of supergene lithiophorite through adsorption has been discussed. Report of Co in terrestrial Mn-ore has opened up new potential in this part of Orissa.

Keywords: Lithiophorite (cobaltian), Manganese ores, Bonai Keonjhar belt, Orissa

Introduction

Lithiophorite \([\text{Al}_2\text{Li}_2\text{OH}_4\text{MnO}_2]\) was first named by Frenzel in 1890 (cited by Fleischer and Faust, 1963) and later confirmed as a valid species by Ramsdell (1932). Wadsley (1952) suggested that it has a layered structure. Subsequently many researchers described it from several parts of the world (Fleischer and Faust, 1963 from Switzerland, Mitchell and Meinitzer, 1967, from Charlottesville, Virginia, Hewett et al. 1968, from Nyecounty, Nevada) Ostwald (1984) demonstrated two varieties of lithiophorite from Australia. Pauling and Kamb (1982) discussed genetic mechanism and crystal structure of lithiophorite. Larson (1970) discussed the genesis of Co and Ni in lithiophorite and cryptomelane from Tennessee. Ostwald (1988) described the cobalt and nickel-rich lithiophorite from Groote Eylandt, Australia. Lithiophorite containing small amount of cobalt, nickel and copper (Fleischer and Faust, 1963, Persiel, 1972) has also been reported from different parts of the world. Presence of lithiophorite in the Precambrian manganese deposits of Orissa is reported by Roy (1981) and Mohapatra et al. (1989). Co in Mn-deposits of Orissa is only recorded by Mohapatra et al. (1989). This short communication is the first report of Co-rich lithiophorite in low-grade Mn-ores of Bonai-Keonjhar belt, Orissa.

Mn-Ore Geology of the Bonai-Keonjhar Belt

The manganese ore bodies in the Bonai-Keonjhar belt are confined to Upper Shale Formation of Precambrian Iron Ore Group. From spatial distribution pattern, these ore bodies can be grouped under three categories: stratiform, stratabound (replacement) and lateritoid type. The stratiform type shows distinct lamination or banding even on mesoscopic scale. The stratabound type is structure-and shear zone-controlled and is often silicified, showing effects of replacement. The lateritoid type occurs as float. Each ore body over its effective area occurs as tabular platform and is capped by a lateritic zone of variable thickness. The manganese ores showing different texture and habit are chemically grouped under high, medium and low grade. Most prominent forms are massive, nodular/oolitic, laminated and spongy/vascular. The ores are mostly associated with shale, predominantly of kaolinitic composition. The ores, in general, show variable proportion of secondary oxy-hydroxide Mn-phases and Fe-phases, with minor clay minerals. The presence of lithiophorite is recorded mainly in low-grade variety, either confined to nodular/oolitic type in lateritic zone or shear-controlled siliceous Mn-ores.

Mineragraphy and Mineral Chemistry

Representative low-grade manganese ore samples
from two associations, viz. lateritic zone and shear zone, were collected and presence of lithiophorite was detected by both optical microscopic and X-ray diffractometric studies. Selective lithiophorite phase in samples from both the associations was also subjected to Electron Probe Micro Analysis (EPMA) by JEOL make JXA 8600 Superprobe, at USIC, Roorkee. Representative samples from three categories of Mn-deposits having lithiophorite were finely powdered and subjected to ICP-MS analysis to obtain the other valuable traces, in addition to Co and Ni.

X-ray diffraction pattern (Fig.1) with distinct sharp peaks at 4.71 Å, 2.37 Å and 9.45 Å confirm the presence of lithiophorite either as a major or minor phase. The mineral has the lowest VHN values (40-60) amongst its coexisting phases. Lithiophorite is present in all categories of ore deposits, especially those of nodular, spongy, laminated and brecciated types. It occurs as a major constituent in nodular and spongy types of lateritoid deposits while in stratiform

Fig.1. X-Ray diffraction pattern of lithiophorite and its associated minerals in different categories of manganese deposits, Bonai-Konjar belt. (a) Lateritoid, (b) Stratiform, (c) Stratabound.
category it forms a minor constituent in the similar morphological types. The associated subordinate minerals in the former category are cryptomelane, and pyrolusite besides minor quartz and illite whereas pyrolusite, cryptomelane and hematite form the major phases in the later category. In the stratabound silicified category, quartz and pyrolusite occurs with subordinate lithiophorite.

Under optical microscope Lithiophorite broadly appears either as vug-filled linings or colloform bands in variable width (Fig. 2). It is characterised by a well-developed bireflection, from pearly grey to brownish grey and by strong anisotropism, making crystallites appear black and white under crossed polars. It occurs as dense masses of micron-sized acicular (Fig. 2a) to pea-shaped crystallines. It also occurs as polyhedral mosaic grains along the periphery of vugs (Fig. 2b). Often, undulose extinction with segmented twinning in mammillary units is noticed (Fig. 2c). In shear zone-controlled stratabound siliceous manganese ore, it forms thinly banded, coarse, radiating crystals, arranged in zig-saw pattern (Fig. 2d).

The EPMA results (Table 1) distinctly indicate the lithiophorite to be Co-bearing. Low level of Co concentration is recorded in the fine-grained variety in which CoO content varies from 0.147 to 0.822% (Table 1, col. 1 to 6). The nodular and spongy samples in lateritoid category (Orahari Mn-deposit, Koira; Table 1, col. 1 to 3) show relatively more Co than similar sample collected from laterite zone capping stratiform deposit (Maidan Mn-deposit, Roida; Table 1, col. 4 to 6). In contrast to the above two categories, the shear zone-controlled siliceous Mn-ore (Shankar Mn-deposit, Barbil) has higher level of Co concentration (CoO: 0.329 to 2.012%). Besides the higher Co content, this coarse-grained variety also shows appreciable Ni (NiO: 0.15 to 1.494%) in its lattice (Table 1, col. 7 to 9).

The results of ICP-MS analysis are shown in Table 2. It is well known that manganese oxides contain some amount of nickel, copper and cobalt. It can be seen from Table 2...
that relative enrichment of other traces like Cu, Ga, Ni, Zn, etc is observed in these samples. Wilson et al. (1970) suggested that Co\textsuperscript{2+} (0.72 Å), Ni\textsuperscript{2+} (0.69 Å) and Zn\textsuperscript{2+} (0.74 Å) would be interchangeable in the lattice. Since lithophorite in stratiform category contains very little Ni, presence of nickel in the bulk sample (Table 2, col 1) may be contributed by some other Mn/Fe mineral.

Mitchell and Meinzer (1967) have reported lithophorite containing 0.2% Li and indicated that a non-lithium containing lithophorite does exist. In the study area, similar results are observed. Lithophorite in two categories of deposits (stratiform and stratabound) contains up to 0.03% Li where as the lateritoid category is almost devoid of lithium (Table 2).

### Discussion

Occurrence of lithophorite mineral in the weathering zone of manganese deposits is well known. It is usually noted in lateritised oolitic material. The present investigation reveals that lithophorite is present as vug filling in nodular and spongy types within lateritic zone and along shear zone in blecciated chert as well. However, both are of supergene in nature as revealed from the textural peculiarities.

Larson (1970) observed that fine-grained variety of lithophorite contains greater amount of Co and Ni than coarse-grained variety. The present investigation reports contrast findings. Lithophorite in the coarse crystalline variety within shear zone contains higher amount of Co and Ni where as the cryptocrystalline variety in pisodite or vuggings has less Co and is almost devoid of Ni. Further, the extent of coalescement in vug-filled type is again related to the magnitude of lateritisation. This is inferred from view of relatively higher level of Co concentration in lithophorite of lateritoid category than that of stratiform types of manganese deposit.

Ostwald (1988) indicated that the lithophorite in lateritised Gooite Eylandt ore has developed by reaction between lateritised manganiferous clays and manganese oxide veins, coatings and disseminations. In the present case, it is assumed that lithophorite is developed at a much later stage, in low-temperature condition from a solution formed due to leaching of Mn and Al minerals, and
subsequently healed-up fracture and/or open spaces within the existing mineral phases. In case of shear zone crystallisation and perfect growth of lithiophorite crystals were possible due to availability of more space. The heavy metals (Co and Ni) got adsorbed, following crystallisation in Mn²⁺.

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