

SHORT COMMUNICATION

Vernadite in Goriajhor Manganese Ores, Gangpur Group, India

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Characteristics of vernadite in manganese ores from Gangpur Group of rocks, Goriajhor Formation, Sundargarh district, Orissa, have been described. This terrestrial vernadite is distinguished from δ -MnO₂ in marine manganese nodules by its well ordered crystallinity and thinner fibrils of submicron size. It appears to be chemically homogenous with the proposed formula: (Ba, K, Fe) MnO₂·nH₂O. This vernadite probably originated through solution, precipitation and redeposition under supergene conditions and later transformed into cryptomelane or romanechite.

Introduction: Vernadite, a hydrated manganese oxide phase was first named by Betekhtin (1937), who considered it as X-ray amorphous. Subsequently, Mikheev (1957) proved it to be crystalline. Burns and Burns (1979), Chukhrov *et al.* (1978, 1980), Chukhrov and Gorshkov (1981) and several others have reported the determinative properties of vernadite. Essential characteristics of Groote Eylandt vernadite have been vividly discussed by Ostwald (1982, 1984, 1985, 1988). Similarity between vernadite and δ -MnO₂ in marine manganese nodules has been indicated by Giovanoli (1980). Although Arrhenius *et al.* (1979) and Giovanoli (1980) have suggested vernadite to be a z-disordered variety of birnessite, a distinction between both the minerals in respect of specific surface area, cation adsorption properties and fibril size have been reported (Benjamin *et al.* 1982).

The manganese ores of Goriajhor region, Sundargarh district, Orissa, predominantly constitute lower oxide manganese minerals (Fermor, 1911; Krishnan, 1937). This is the first report of the mineral vernadite in the Gangpur Group of rocks of Precambrian age (946-846 Ma). This paper outlines some diagnostic characteristics of vernadite and discusses its genesis in the Goriajhor manganese deposit.

Mineralogy: Goriajhor vernadite is crystalline, shows low optical reflectance (8-10% in 546 nm, in air), low VHN (60-80) and is characterised by strong XRD peaks at 2.39Å, 3.11Å and 1.42Å, followed by medium peaks at 1.83Å, 1.65Å, 1.54Å and 4.91Å (Fig.1). This vernadite lacks XRD lines at 2.45Å, 2.20Å, and 2.15Å as observed by Mikheev (1957) and Chukhrov *et al.* (1980). Other associated minerals with Goriajhor vernadite are jacobsonite, magnetite, spessartine and quartz.

Vernadite, in general, occurs as minute ooids (Av. 70µ dia; Pl. 1.3). These ooids often join together to form polyooids (Pl. 1.4). The mineral shows low relief and appears like clay minerals under the optical microscope (Pl. 1.1). However, in higher magnification through scanning electron microscopy, each ooid is found to comprise curved and crenulated fibrils of sub-microscopic dimension (Av. 1 to 2µ; Pl. 1.5). The fibrils of vernadite are tens of micron smaller than that of the flakes of birnessite.

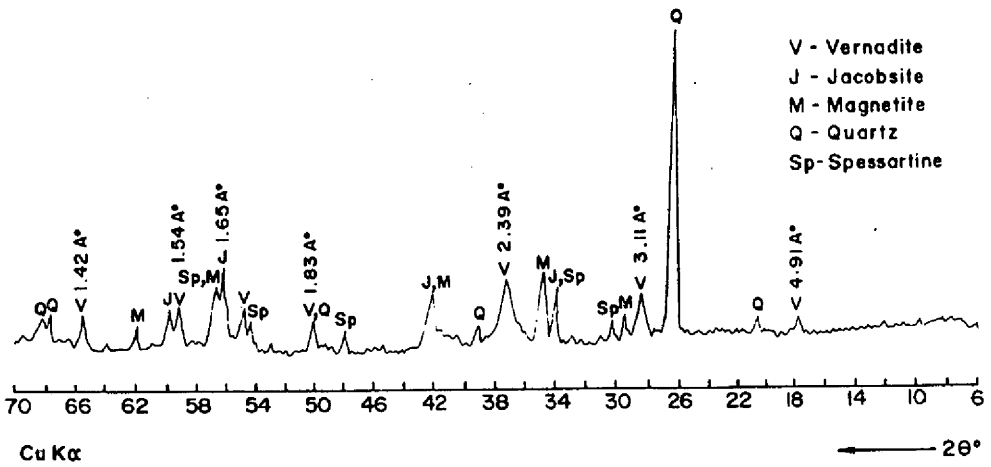


Fig.1. X-ray diffraction pattern of vernadite associated with jacobsonite, magnetite, spessartine and quartz in Goriajhor manganese ores.

Chemistry: The chemical composition of vernadite in five optically alike samples was determined using CAMECA electron probe (by fully ZAF-corrected EPMA). The results (Table-I) are almost in consistent with that of Burns and Burns (1979) and Ostwald (1988)

Table I. Electron Probe Microanalysis of Vernadite (Wt.%)*

	1	2	3	4	5	6	7	8	9
SiO ₂	0.11	0.14	0.09	0.13	0.10	0.7	0.4	0.6	0.3
Al ₂ O ₃	1.22	1.80	1.54	1.51	1.35	3.0	2.4	2.2	1.5
Fe ₂ O ₃	4.22	5.12	4.08	3.66	4.45	4.2	2.1	3.3	2.2
MnO ₂	67.79	66.64	68.86	70.56	66.25	60.6	61.7	62.7	65.3
MgO	0.01	0.03	-	0.04	0.06	0.9	0.9	0.6	0.9
CaO	0.43	0.48	0.40	0.46	0.41	0.2	0.2	0.2	0.3
Na ₂ O	0.03	0.05	0.14	0.10	0.07	0.3	0.2	0.4	0.3
K ₂ O	3.41	2.86	3.33	2.71	2.05	1.1	1.2	1.2	1.5
BaO	4.17	4.28	4.57	6.08	5.17	2.3	3.0	5.0	4.0
NiO	0.05	0.02	0.02	0.11	0.10	ND	ND	ND	ND
H ₂ O ⁺	18.56	18.58	16.97	14.64	19.99	26.7	27.9	23.8	23.7

*1 to 5 : Goriajhor, India; 6 to 9 : Groote Eylandt, Australia (Ostwald, 1988)

ND : Not detected by EPMA; H₂O⁺ by difference.

for terrestrial vernadite. The X-ray image map (Pl.2) distinctly demonstrates that vernadite is an aggregate of crystallites of sub-micron size with almost uniform chemical composition. Unlike marine manganese nodules in which the alternate dark (Ferrihydrite or ferroxhyte) and bright (δ -MnO₂ = vernadite) concentric layers are of different composition, the fibrils in this terrestrial vernadite do not show such compositional heterogeneity. The constant association of Ba, K and Fe with the manganese oxide suggests a general formula (Ba, K, Fe) MnO₂.nH₂O. The low concentration of Ca and Ni is significant and indicative of its high cation adsorption

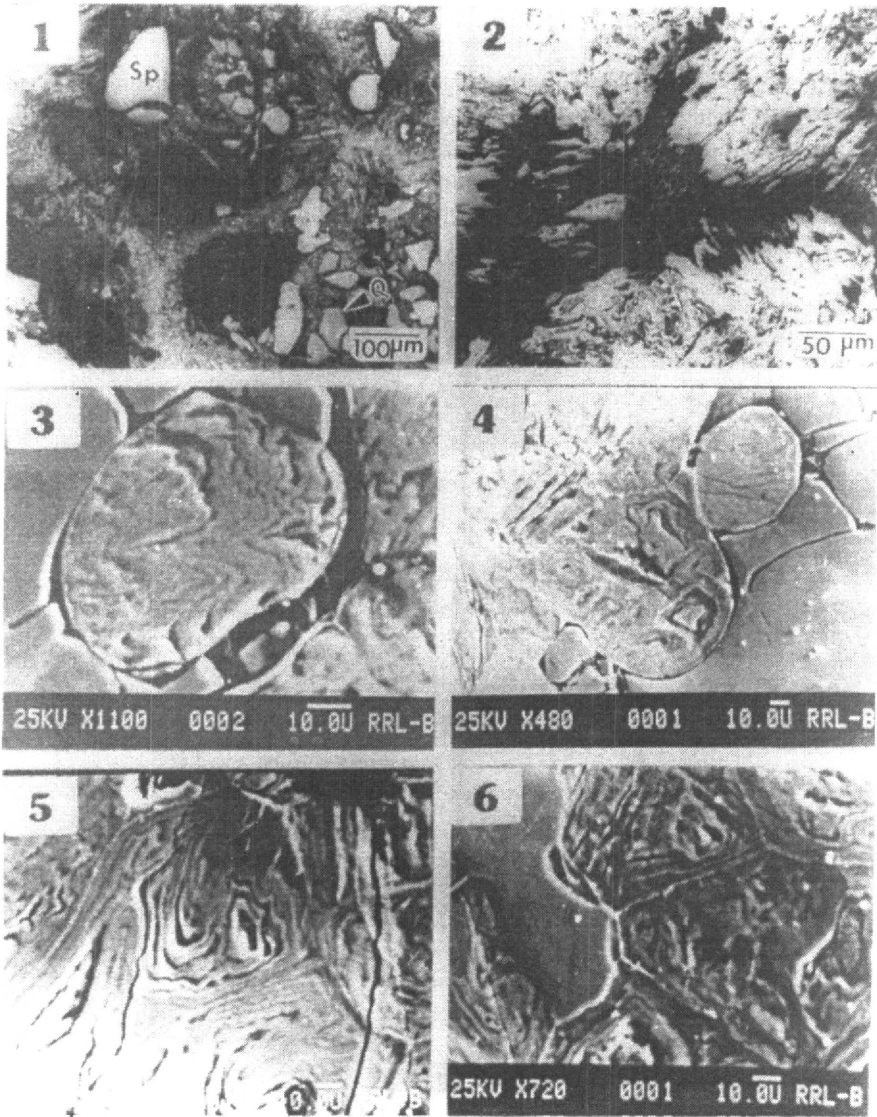


Plate 1. 1.1 - Vernadite (black and grey) associated with quartz (q) and spessartine (Sp). Pol. light.
 1.2 - Vernadite occurring as fine crystallites arranged in radiating or concentric pattern. Pol. light.
 1.3 - Scanning electron micrograph of vernadite ooid.
 1.4 - Fusion of vernadite ooids leading to a polyooidal structure.
 1.5 - Enlarged view of vernadite showing well developed concentric layers.
 1.6 - Growth of cryptomelane at the expense of vernadite.

properties. Minor amount of alumina (< 2%) may be an impurity in vernadite. The total value in the range of 85-80% reveals a water content (both absorbed and structural) of 15-20% in vernadite. The high cation adsorption properties of Goriajhor vernadite ($MnO_2/$

cations=4.5 to 5) is in contrast to the value ($MnO_2/R_2O + R_2O_3 = 2.84$) proposed for a terrestrial vernadite by Chukhrov *et al.* (1978).

Genesis: In Goriajhor Mn-deposit, a secondary origin of vernadite mineralisation is well revealed from its textural peculiarities. Vernadite is considered to have been formed through colloidal precipitation during supergene processes. The major phases in the protore are spessartine, jacobsite and braunite with minor barite. Mn-evolution from the protore,

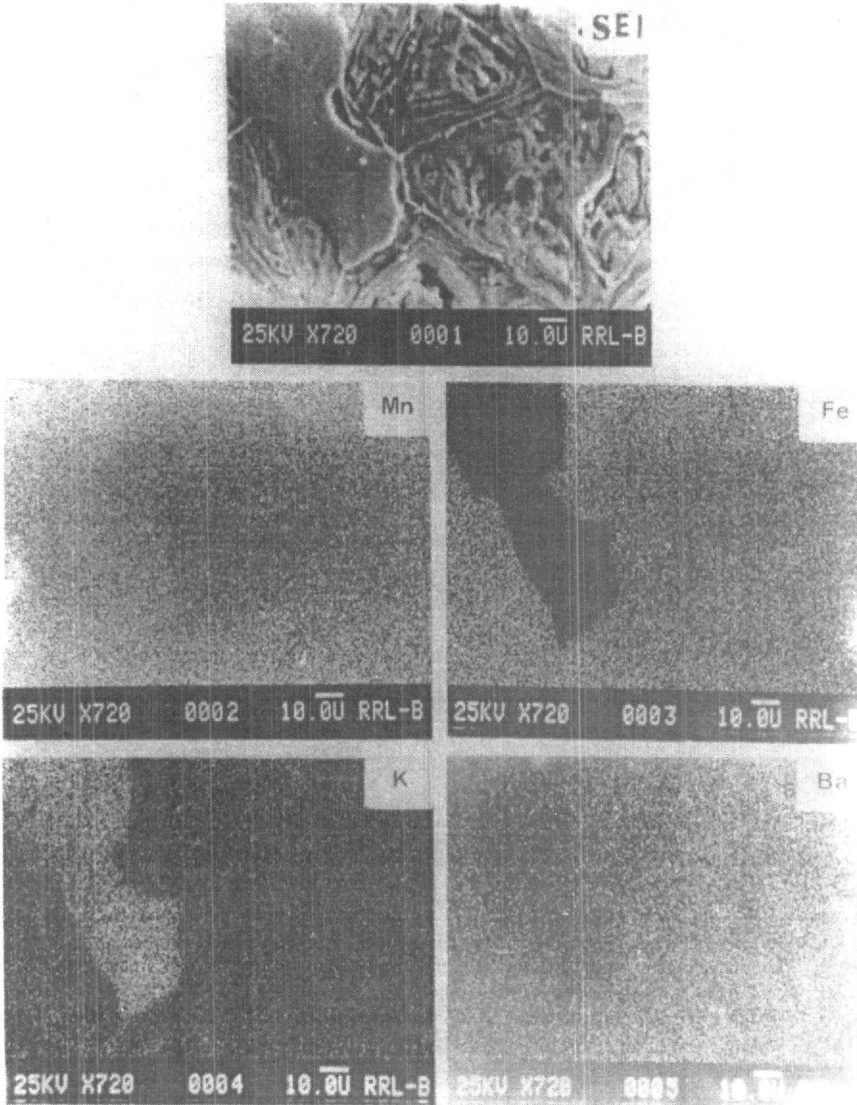


Plate 2. X-ray image map of Mn, Fe, K and Ba elements in the area shown in plate 1.6.

therefore, may be attributed to the hydrolysis of Mn-garnet. Most likely the remobilised circulating mineralising solution gets redeposited as minute ooids in the favourable sites of host manganese bearing/gonditic rocks. These ooids subsequently fuse together (Pl. 1.4) and adsorb other cations under suitable Eh-pH conditions. The source of barium in the vernadite structure may be due to precursor barite often noticed in the protore. However, further oxidation transforms these hydrated manganese oxides into higher oxide minerals such as cryptomelane and/or romanechite. Plate.2 illustrates the growth of cryptomelane at the expense of vernadite. The possibility of microbiological origin of vernadite as invoked by Chukhrov (1978) and Ostwald (1981a) in some manganese deposits does not appear feasible in Goriajhor Mn-ores.

Conclusion: Vernadite in Goriajhor ores show a distinct mineralogy, chemical composition and textural peculiarity. It has concentric crenulated fibrils which are much smaller in size than that of birnessite. Vernadite is different from δ -MnO₂ by its higher degree of crystallinity and uniform chemical composition. Because of definite chemistry, better crystallinity and well defined morphology, the authors suggest to retain the mineralogical terminology "Vernadite" rather than using chemical designation δ -MnO₂. Vernadite can probably be considered as an intermediate phase between the original Mn(OH) sols and cryptomelane/romanechite formed in an oxidising environment.

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References

- ARRHENIUS, G., CHEUNG, K., CRANE, S., FISH, M., FRAZER, J., KORKISCH, J., MELLIN, T., NAKAO, S., TSAI, A., and WOLD, G. (1979). Counterions in marine manganates. In: C.Lalou (Editor), *La Genes des nodules de manganese*, C.N.R.S. No.289, pp.333-356.
- BENJAMIN, W.H., STEPHEN, L.L., and DAVID, C.B., (1982). Bureau of Mines Information Circular, United States Dept. of the Interior, U.S.A.
- BETEKHTIN, A.G. (1937). New Mineral Species of the Group of Manganese Hydroxides. *Zap. Vaes, Min. Obh.*, v.66, pp. 4-8.
- BURNS, R.G., and BURNS, V.M. (1979). Manganese oxides, In: R.G.Burns (editor), *Marine Minerals*, Min. Soc. Am., Short Course Notes, v.6, pp.1-40.
- CHUKHROV, F.V., and GORSHKOV, A.I. (1981). Iron and Manganese oxide Minerals in Soils. *Trans. R. Soc. Edinburg*, v.72, pp.195-200.
- CHUKHROV, F.V., GORSKOV, A.I., RUDNITSKAYA, E.J., BERESOVSKAYA, V.V., and SIVSTOV, A.V. (1978). Vernadite, *Izv. Akad. Nauk, SSSR*, v.6, pp. 5-19.
- CHUKHROV, F.V., GORSKOV, A.I., RUDNITSKAYA, E.S., BERESOVSKAYA, V.V., and SIVSTOV, A.V. (1980). Manganese Minerals in Clays: A Review. *Clays and Clay Miner.*, v.28, pp.346-354.
- FERMOR, L.L. (1911). Notes on the Manganese -Ore Deposits of the Gangpur State, Bengal and on the distribution of the Gondite Series in India. *Rec. Geol. Surv. India*, v.41, pp. 12-21.
- GIOVANOLI, R. (1980). Vernadite is random-stacked birnessite. *Miner. Deposita*, v.15, pp.251-253.
- KRISHNAN, M.S. (1937). The Geology of Gangpur State (Eastern States). *Mem. Geol. Surv. India*, v.71, pp. 133-143.
- MIKHEEV, V.I. (1957). *Text Book on X-ray Analysis*, Leningrad, 642pp.
- OSTWALD, J. (1981a). Evidence for a biogeochemical origin of the Groote Eylandt manganese ores. *Econ. Geol.*, v.76, pp. 556-567.

- OSTWALD, J. (1982). Characterisation of Groote Eylandt manganese minerals. BHP Tech. Bull., v.26, pp.52-56.
- OSTWALD, J. (1984). Vernadite - a possible hybrid structured mineral. Aust. Mineral., July, pp. 269-271.
- OSTWALD, J. (1985). Mineralogy of battery-active manganese ore from Groote Eylandt. In: W.C. Park (Editor), Appl. Mineral., A.I.M.E., pp. 1095-1108.
- OSTWALD, J. (1988). Mineralogy of the Groote Eylandt Manganese Oxides : A Review Ore Geo. Rev., v.4, pp.3-45.

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