

AKHTENSKITE—THE NATURAL ANALOG OF ϵ -MnO₂

F. V. Chukhrov*, A. I. Gorshkov, A. V. Sivtsov, V. V. Berezovskaya, Yu. P. Dikov,
G. A. Dubinina, and N. N. Varinov

Translated from "Akhtenskit—prirodnyy analog ϵ -MnO₂," *Izvestiya AN SSSR, seriya geologicheskaya*, 1989, No. 9, pp. 75-80. The authors are with the Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry [IGEM] of the USSR Academy of Sciences. They present the formal description of this new mineral, a structural analog of feroxyhyte δ' -FeOOH. Data are given on akhtenskite from its type locality, the Akhtenskoye limonite deposit in the South Urals, and from a second locality, Mt. Zarod in Sikhote Alin. Natural oxidation of Mn to form a phase as unstable as ϵ -MnO₂ must be a process more rapid than can be accomplished inorganically, but experiments show it is easily accomplished by bacterial action.

In 1951 Kondrashev and Zaslavskiy [2] synthesized a new phase, MnO_{1.97} with 5.3% water, by oxidizing Mn²⁺ in a solution of Mn(NO₃)₂ in 2 HNO₃ using calcium chlorate as an oxidizing agent. The structure proposed for this phase, based on its x-ray diffraction pattern, had a hexagonal very dense packing of oxygen atoms and a statistical distribution of Mn⁴⁺ over half of the octahedral positions. The dimensions of the hexagonal unit cell where $a_0 = 2.786 \pm 0.001$ Å and $c_0 = 4.412 \pm 0.01$ Å; the space group was D_{6h}⁴-P6₃/mmc (C6/mmc). Kondrashev and Zaslavskiy suggested the name ϵ -MnO₂ for this phase. They also suggested that ϵ -MnO₂ differs sharply in diffraction features and, correspondingly, in unit cell dimensions and symmetry, from pyrolusite, cryptomelane, ramsdellite and γ -MnO₂ with imperfect structure.

In 1978 de Wolff et al. [11] published data on ϵ -MnO₂; the hexagonal unit cell edges of their phase were $a_0 = 2.80$, $c_0 = 4.45$ Å.

We first identified a natural analog of artificial ϵ -MnO₂ by transmission electron microscopy in a specimen of psilomelane from the Akhtenskoye limonite deposit in the South Urals [7, 10] (specimen was obtained from the museum of the Leningrad Mining Institute). In this sample, ϵ -MnO₂ forms fine light gray or black mixtures with cryptomelane and nsutite, in which the individual components are

indistinguishable macroscopically or under the binocular microscope. It was not possible to separate a pure phase of ϵ -MnO₂ for chemical analysis. Its analogy in structure and composition to the artificial oxide ϵ -MnO₂ is based entirely on the electron microdiffraction, x-ray photoelectron spectroscopy and energy-dispersive analysis. The energy-dispersive spectra of different particles and aggregates of the ϵ phase from the Akhtenskoye deposit show manganese as the only cation (inset in Fig. 1). X-ray photoelectron investigation of natural ϵ -MnO₂ made it possible to establish that it contains tetravalent manganese and oxygen; no OH group or molecular water were found. Two varieties of todorokite ($a_0 = 19.5$ and $a_0 = 2.44$ Å) and goethite were identified by electron microdiffraction in several samples containing ϵ -MnO₂, and pyrolusite in one sample.

In electron microscope images, ϵ -MnO₂ from the Akhtenskoye deposit consists mainly of aggregates of relatively small platy particles with a basal (001) face. In many aggregates, the laminae are strictly parallel to one another. Therefore diffraction patterns obtained from these aggregates are practically points (inset in Fig. 1). This can be explained by the fact that the flaky aggregates of oriented particles of natural ϵ -MnO₂ formed by alteration of another mineral. This conclusion is based on an electron microscope image (Fig. 1) in which flakes of ϵ -MnO₂ form three systems of straight rows at angles of 120° to each other. Such rows of flakes apparently are formed as a result of replacement of a hexagonal

*Deceased.

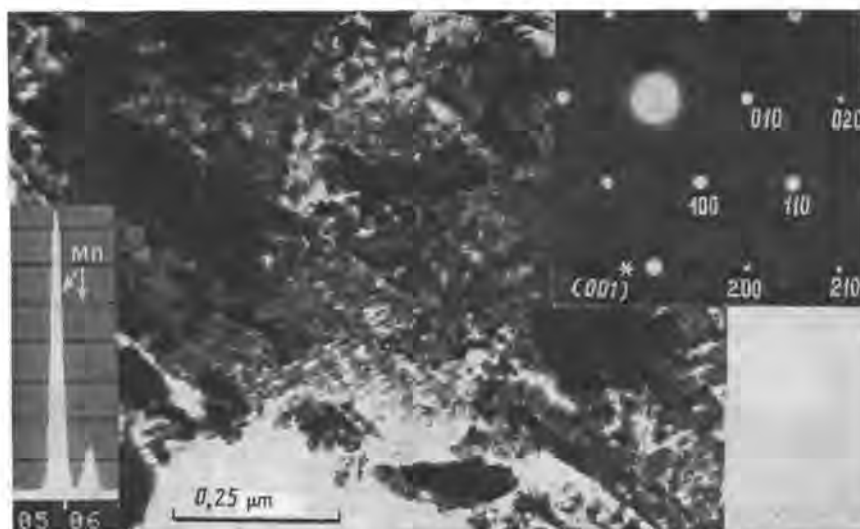


FIGURE 1. Electron microscope image of akhtenskite from the Akhtenskoye deposit. In inserts: diffraction pattern showing the (001)* plane of the reciprocal lattice and energy-dispersive spectrum.

(trigonal) mineral along the (001) plane. That mineral could be a manganiferous carbonate. Cleavage parallel to the (001) plane probably also produces the appearance of a unique microaggregate of a monocrystalline type of ϵ -MnO₂ (Fig. 1).

Electron-diffraction patterns (one of them is shown in the inset in Fig. 1) were obtained from particles of natural ϵ -MnO₂; they show the various planes of its reciprocal lattice [7]. Calculation from these patterns made it possible to determine the hexagonal cell parameters unambiguously ($a_0 = 2.85$; $c_0 \approx 4.48$ Å); they are very close to those of synthetic ϵ -MnO₂.

The cell dimensions are consistent with the idea that a_0 is approximately equal to the edge of the base of an Mn⁴⁺ octahedron and c_0 corresponds to the height of two octahedra, i.e., to the thickness of two layers of hexagonal, very densely packed oxygen anions. The two-layered hexagonal manganese minerals—feitknechite (β -MnOOH) and pyrochroite (Mn(OH)₂)—have larger cell dimensions: $a_0 = 3.17$, $c_0 = 4.62$ Å (ASTM, No. 18804) and $a_0 = 3.315$, $c_0 = 4.72$ Å (ASTM, No. 12696), respectively.

For a more rigorous substantiation of the correspondence of our phase with artificial ϵ -MnO₂, we analyzed the intensity of hkl reflections on the electron-diffraction patterns [7]. The intensities of

the reflections $J_E(hkl)$, measured on several patterns, were compared with the theoretical values $J_T(hkl)$ calculated from the structural model of ϵ -MnO₂ [7]. The atoms of this oxide are arranged in the structure according to the rule $A_{0.5c}B_{0.5c}A_{0.5c}B...$, where A and B are the positions of anions in the very dense hexagonal packing, c is the position of Mn⁴⁺ in the octahedra (at 0.5 their height), and the coefficient 0.5 characterizes the extent of statistical filling of the octahedra by manganese atoms.

$J_T(hkl)$ was calculated from the formula $J_T(hkl) = F_T^2(hkl)d(hkl)$, where $F_T(hkl)$ is the structure factor and $d(hkl)$ is the interplanar spacing (correction for mosaic structure). Comparison of $J_T(hkl)$ with $J_E(hkl)$ [7] showed fairly good qualitative agreement. This made it possible to substantiate the structural model and say that the manganese mineral from the Akhtenskoye deposit is identical to the synthetic phase of ϵ -MnO₂. Like the latter, it belongs to the space group D_{6h}^4 -P6₃/mmc (C6/mmc). It can be assumed that the slightly higher a_0 dimension in the natural ϵ -MnO₂ is related to small amounts of larger divalent or trivalent manganese ions entering into its structure.

In 1983 the natural ϵ -MnO₂ phase was recognized by the Commission on New Minerals and Mineral Names of the IMA as a new mineral, with the name "akhtenskite."

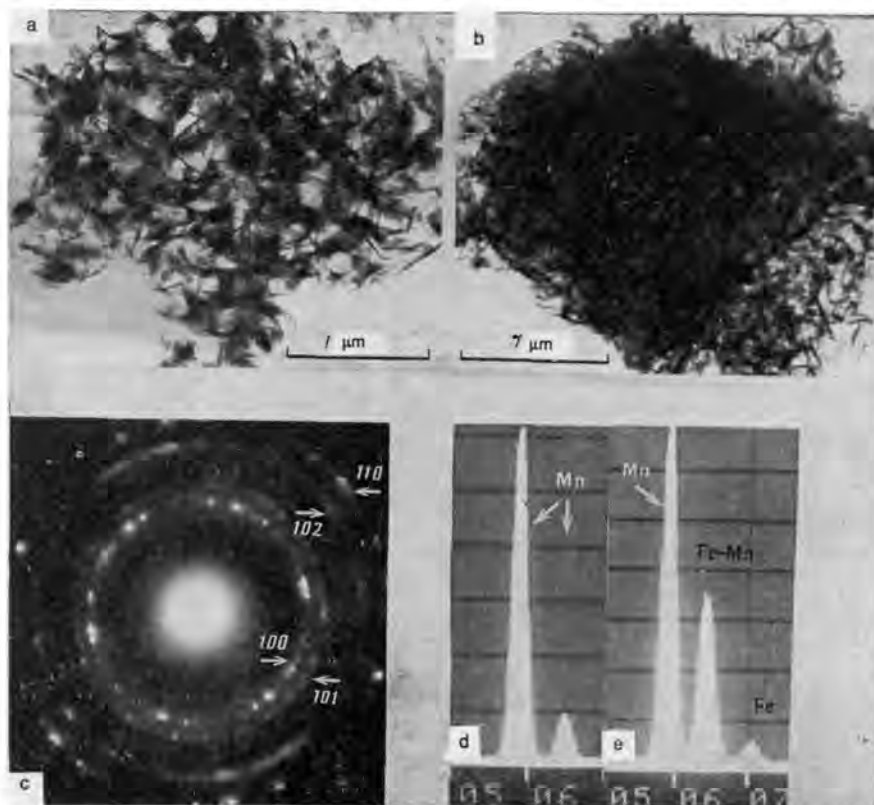


FIGURE 2. a, b) Electron microscope images of fine flaky aggregates of akhtenskite from Mt. Zarod; c) electron-diffraction patterns from more coarse-flaky aggregate of the mineral; d, e) energy dispersive spectra of akhtenskite (d) and Fe-akhtenskite (e).

We identified akhtenskite and its variety Fe-akhtenskite (using the analytical electron microscope) from a new locality, Mt. Zarod in Sikhote Alin, where it occurs in ferromanganese encrustations on high-titanium oceanic basalt. The sample was kindly sent to us by A. I. Khanchuk, who considers Mt. Zarod to be a Permo-Carboniferous guyot.

Akhtenskite and the fine association of Fe-akhtenskite and iron-free vernadite found with it form a thin (0.3 mm) crust on the surface of a ferromanganese encrustation consisting of poorly crystallized zinc-bearing busserite-1. The akhtenskite and the Fe-akhtenskite consist of fine flaky polycrystalline aggregates (Fig. 2a, b). Aggregates consisting of larger flakes are better crystallized than the fine-flaky ones, as electron-diffraction patterns indicate. For this akhtenskite, each pattern usually shows four rings (Fig. 2c) with $d = 2.45$ (hkl 100), 2.15 (101),

1.65 (102) and 1.42 Å (110). These interplanar distances, calculated from the diffraction patterns, unequivocally correspond to the hexagonal unit cell typical of akhtenskite [7], with the dimensions $a_0 = 2.83 \pm 0.03$; $c_0 = 4.47 \pm 0.03$ Å. Cell edges for Fe-akhtenskite are practically the same.

The energy-dispersive spectra obtained from akhtenskite show only a manganese peak (Fig. 2d), peaks of Mn and Fe (Fe/Mn = 0.1-0.3) are seen on the spectra of Fe-akhtenskite. The formula for Fe-akhtenskite can be written in the form $(Mn_{1-x}Fe_x)O_{2-x}(OH)_x$.

Morphologically the fine-flaky aggregates of akhtenskite from Mt. Zarod (Fig. 2a, b) are practically identical to those of Fe-vernadite and Mn-feroxyhyte of oceanic hydrogenic ferromanganese nodules [3] and crusts. Both these minerals have a

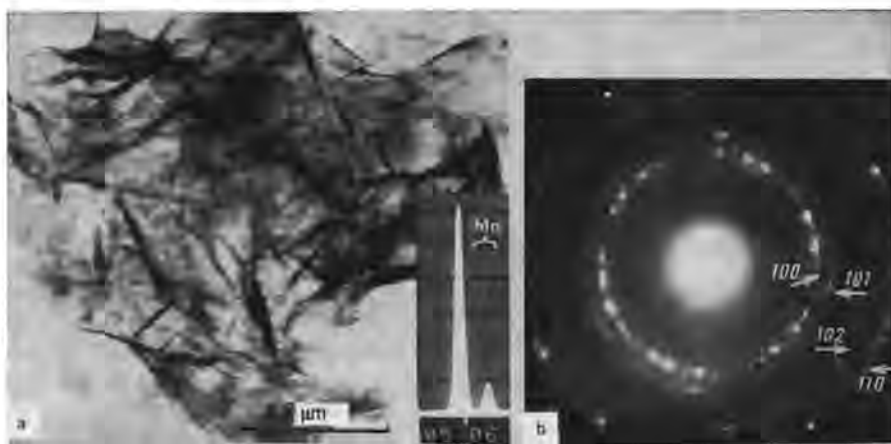


FIGURE 3. a) Electron microscope image of biogenic fine-flaky aggregate of ϵ - MnO_2 ; in inset—energy dispersive spectrum; b) electron-diffraction from an aggregate of biogenic akhtenskite.

pseudolayered structure, and feroxyhyte [5] is a structural analog of akhtenskite [7]. Vernadite, as well as the association of Fe-vernadite with feroxyhyte [9], is easily formed [6, 9] as a result of the activity of Fe- and Mn-oxidizing bacteria (*Metallogenium* and several others). These bacteria are strong catalysts, therefore these minerals form very rapidly and have disordered structures.

The idea of a biogenic origin of the akhtenskite from Mt. Zarod occurred to us. To check the possibility of obtaining akhtenskite biogenically, we conducted laboratory experiments using a manganese-oxidizing microorganism of the genus *Metallogenium*. As is known, this organism is very widespread in freshwater and marine habitats and in manganese deposits, both Recent and ancient [1, 4, 12, 13], manganese ores [4, 12]. In our experiments we used a binary culture of *Metallogenium* D-405 with a microscopic asporogenic fungus *Mycelium sterilium*. For the accumulation of manganese, *Metallogenium* was cultured in a sterile medium consisting of 1 g hydrolyzed starch, distilled water, or sea water diluted with distilled in the proportion of 1:1-1000 ml, 2 g manganese carbonate suspension (pH = 7.5), and MnCO_3 , the artificial analog of rhodochrosite; this was mixed with equimolar solutions of MnSO_4 and NaHCO_3 . The precipitate was carefully washed with several batches of distilled water. Oxidation of the manganese carbonate under the influence of *Metallogenium* under conditions resistant to chemical oxidation by dissolved oxygen,

began the next day. The divalent manganese introduced into the medium was completely oxidized by the bacteria in a few days. In control without bacteria under sterile conditions, the manganese was not oxidized and no oxides were formed, even after several months exposure.

Samples of the manganese oxide produced in these experiments were studied by analytical electron microscopy, images, energy dispersive spectra and electron-diffraction patterns from various particles successively obtained. Fine-flaky aggregates of ϵ - MnO_2 were recorded in the samples of oxides obtained as described above (Fig. 3a); the only cation the aggregates contained was manganese (inset, Fig. 3a). Diffraction patterns obtained from the fine-flaky aggregates of ϵ - MnO_2 (Fig. 3b) consisted of annular reflections with $d = 2.43, 2.14, 1.64$ and 1.41 Å. From these interplanar distances, the hexagonal unit cell dimensions were obtained: $a_0 = 2.81 \pm 0.03$, $c_0 = 4.45 \pm 0.03$ Å.

The conditions under which biogenic ϵ - MnO_2 were obtained indicate that it is formed when Mn^{2+} is oxidized very rapidly to Mn^{4+} . Inorganic (abio-genic) oxidation of manganese, with such rapid formation of an unstable phase like akhtenskite is inconceivable in nature. At the same time, as the experiments show, it is quite permissible to postulate a relationship between the oxidation of manganese to form akhtenskite and bacterial action, in contrast to what was believed earlier [7].

Conclusion

A new manganese oxide, akhtenskite (ϵ -MnO₂; Akhtenskoye deposit, South Urals) is described; it is a structural analog of feroxyhyte (δ' -FeOOH). The structure is based on hexagonal, very dense packing of oxygen atoms with Mn⁴⁺ atoms distributed statistically over half of the octahedral positions. The dimension of the hexagonal unit cell are $a_0 = 2.85 \pm 0.02$ Å, $c_0 = 4.48 \pm 0.03$ Å.

Data are given of detailed analytical electron microscope study of akhtenskite and its variety Fe-akhtenskite from a second locality at Mt. Zared in Sikhote Alin.

Successful experiments to obtain ϵ -MnO₂ biogenically, by rapid reaction oxidation of Mn²⁺ to Mn⁴⁺, are described. The experiments suggest that the oxidation of manganese to form akhtenskite in nature is related to bacterial action.

References

1. Balashova, V. V. and Dubinina, G. A., 1988, Microorganisms that oxidize iron and manganese. In *Khemolitotrofnyye mikroorganizmy (Chemolithotrophic Microorganisms)* (pp. 101-122): Nauka Press, Moscow.
2. Kondrashov, Yu. D. and Zaslavskiy, A. I., 1951, Structure of manganese dioxide modifications: *Izvestiya AN SSSR, seriya fizicheskaya*, Vol. 15, No. 2, pp. 179-186.
3. Uspenskaya, T. Yu., Gorshkov, A. I., and Sivtsov, A. V., 1988, Structure and mineral composition of oceanic nodules: *Izvestiya AN SSSR, seriya geologicheskaya*, No. 4, pp. 88-97 [translated in *International Geology Review*, Vol. 30, No. 2, pp. 216-225, 1988].
4. Perfil'yev, B. V. and Gabe, D. R., 1964, *Rol' mikroorganizmov v obrazovanii zhelezomargantsevykh ozernykh rud (The Role of Microorganisms in the Formation of Lacustrine Ferromanganese Ores)* (pp. 6-53): Nauka Press, Moscow.
5. Chukhrov, F. V., Zyragin, B. B., Gorshkov, A. I., et al., 1976, Feroxyhyte—a new modification of FeOOH: *Izvestiya AN SSSR, seriya geologicheskaya*, No. 4, pp. 88-978.
6. Chukhrov, F. V., Gorshkov, A. I., Rudnitskaya, Ye. S., et al., 1978, On vernadite: *Izvestiya AN SSSR, seriya geologicheskaya*, No. 6, pp. 5-19.
7. Chukhrov, F. V., Gorshkov, A. I., Sivtsov, A. V., et al., 1982, A natural analog of synthetic ϵ -MnO₂: *Izvestiya AN SSSR, seriya geologicheskaya*, No. 1, pp. 56-65.
8. Chukhrov, F. V., Drits, V. A., Gorshkov, A. I., et al., 1987, Structural models of vernadite: *Izvestiya AN SSSR, seriya geologicheskaya*, No. 12, pp. 3-15 [translated in *International Geology Review*, Vol. 29, No. 11, pp. 1337-1347, 1987].
9. Chukhrov, F. V., Gorshkov, A. I., Sivtsov, A. V., and Dubinina, G. A., 1988, Biogenic formation of vernadite-feroxyhyte associations. In *Tez. XIII Vsesoyuz. shkoly po morskoy geologii (Abstracts, XIII All-Union School of Marine Geology)* (Vol. 4, pp. 197-198): Inst. Okeanologii AN SSSR, Moscow.
10. Chukhrov, F. V., Gorshkov [Gorshkov], A. I., Sivtsov, A., Dickov [Dikov], Ju. [Yu.] P., and Verezhovskaja [Berezovskaya], V. V., 1982, The natural occurrence of ϵ -MnO₂: *Chemie der Erde*, No. 41, pp. 237-239.
11. de Wolff, P. M., Wissler, J. W., Giovanoli, R., and Brüttsch, 1978, Ueber ϵ -Mangandioxid: *Chimia*, Vol. 32, No. 7, pp. 257-259.
12. Dubinina, G. A., 1981, The role of microorganisms in the formation of the recent iron-manganese lacustrine ores. In *Geol. Geochem. of Manganese* (Vol. VIII, pp. 305-326): Hungarian Acad. Sciences Publishing House, Budapest.
13. Muir, M. D., 1978, Microenvironments of some modern and fossil iron- and manganese-oxidizing bacteria. In Krumbein, N. E. (Ed.), *Environmental Biogeochemistry and Geomicrobiology* (Vol. 3, pp. 937-946): Ann Arbor Science Publishers.