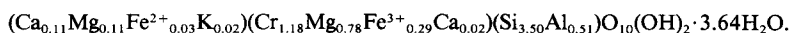


REASSESSMENT OF THE VOLKONSKOITE-CHROMIAN SMECTITE NOMENCLATURE PROBLEM

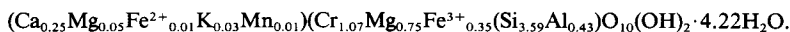
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Abstract—The name volkonskoite was first used in 1830 to describe a bright blue-green, chromium-bearing clay material from the Okhansk region, west of the Ural Mountains, U.S.S.R. Since that time, the name has been applied to numerous members of the smectite group of clay minerals, although the reported chromium content has ranged from 1% to about 30% Cr₂O₃. The name has also been applied to some chromian chlorites. Because volkonskoite has been used for materials that differ not only in their chromium content but also in their basic structure, the species status of the mineral has been unclear.

To resolve this uncertainty, two specimens of volkonskoite from (1) Mount Efimiatsk, the type locality in the Soviet Union (USNM 16308) and (2) the Okhansk region in the Perm Basin, U.S.S.R. (USNM R4820), were examined by several mineralogical techniques. Neotype sample 16308 has the following structural formula:



Sample R4820 has the following structural formula:



Mössbauer spectroscopy indicates that 91% and 98% of the iron is present as Fe³⁺ in samples 16308 and R4820, respectively. X-ray powder diffraction patterns of both samples have broad lines corresponding to minerals of the smectite group.

On the basis of these data, volkonskoite appears to be a dioctahedral member of the smectite group that contains chromium as the dominant cation in the octahedral layer. Smectites containing less than this amount of octahedral chromium should not be called volkonskoite, but should be named by chemical element adjectives, e.g., chromian montmorillonite, chromian nontronite.

Key Words—Chlorite, Chromium, Nomenclature, Octahedral cations, Smectite, Volkonskoite.

INTRODUCTION

In 1981 one of the authors (D.R.S.) collected a bright blue-green clay from the Lucky Hill pit, Candelaria mine, Mineral County, Nevada. This clay was subsequently identified as a smectite containing slightly more than 3 wt. % Cr. In attempting to give a mineral name to this material, the authors encountered the confusing and often conflicting literature on volkonskoite and other chromium-bearing smectites. This report re-examines the terminology and nomenclature of such chromium-bearing smectite.

The name volkonskoite (also spelled volchonskoite, wolchonskoit, and volkhonskoite) was given to a chromium-bearing, dioctahedral smectite in about 1830 (see below). Cr is an effective chromophore in that only a small amount is required to give an intense color to its host mineral. Perhaps for this reason, many smectites were called volkonskoite in the literature even though their Cr content was minor. Many of these species were also impure and poorly characterized. Despite the longevity of the name, but perhaps because of the low Cr contents of many materials so described, some reference texts (e.g., Fleischer, 1983) do not consider volkonskoite to be a valid mineral species.

Brindley (1980) recognized the nomenclature problem and stated that volkonskoite is properly used only

if Cr is the dominant octahedral cation present; the Cr₂O₃ content is then likely to exceed 15 wt. %. By this criterion, the majority of the "volkonskoites" described in the literature are more properly termed chromian montmorillonite or chromian nontronite, or are mixtures of various chromium-bearing minerals.

On the basis of a re-examination of type volkonskoite from Efimyatsk in the Okhansk region of the Perm Basin, U.S.S.R., and a study of literature descriptions of such Cr-bearing smectites, a definition of volkonskoite as a mineral species has emerged. This definition was approved in advance by the International Mineralogical Association Commission on New Minerals and New Mineral Names.

REPORTED OCCURRENCES AND PREVIOUS WORK

History of the nomenclature problem

Khoury *et al.* (1984) and particularly Mackenzie (1984a, 1985) discussed the early history of the discovery and characterization of volkonskoite from the Okhansk region, in the Soviet Union. Although Mackenzie (1984a) correctly observed that most standard texts attribute the first description of the mineral volkonskoite to Kämmerer (1831) and noted that the mineral was first described in 1830, some important in-

formation may be added. Krotov (1902) acknowledged that volkonskoite was discovered in 1830, and Kryzhanovskii (1928) cited several references that made mention of this fact. Aleksandrov *et al.* (1940) described a first period of investigation of volkonskoite from 1830 to 1850 and quoted an anonymous article from the 1830 *Gornyi Zhurnal* that was also mentioned by Mackenzie (1984a). Borisenko and Borisenko (1962) stated that "Despite the fact that the first reference to volkonskoite, published in the *Gornyi Zhurnal*, dates to the year 1830, to the present time there remains a series of controversial questions linked with the mineralogy and genesis of this mineral." Much of the later geologic and mineralogic information on this mineral has been published in the Soviet Union (e.g., Aleksandrov *et al.*, 1940; Borisenko and Borisenko, 1962; Gudoshnikov *et al.*, 1968; Kultyshev, 1938).

Reported occurrences

The anonymous report in 1830 (quoted in Aleksandrov *et al.*, 1940; Borisenko and Borisenko, 1962; and Mackenzie, 1984a) gave the type locality of volkonskoite as Mount Efimyata (see, e.g., Kokscharov, 1853) near the village of Efimyata (see Aleksandrov *et al.*, 1940) in the Okhansk district, middle Kama River area, west of Perm, on the west side of the Ural Mountains. Kämmerer (1831) noted the occurrence of the mineral, but the first complete analysis appears to have been made by Berthier in 1833 (see Kersten, 1839). Kokscharov (1853) summarized analyses reported by Kersten in 1839, by Ilimov in 1842, and by Ivanov in 1851. Additional occurrences of volkonskoite were later found in the surrounding Permian calcareous sandstones of the Perm Basin and were summarized in what is probably the most comprehensive single work by Aleksandrov *et al.* (1940) on the occurrences in the Kama River and Udmurtia (formerly Vyatka) regions. Only some of the Soviet literature on these materials is discussed in the present paper. For additional information, the reader is referred to references in the papers cited herein.

Volkonskoite from the Kama area red beds, as well as other Cr-bearing smectites from other parts of the Perm Basin, the Caucasus Mountains, and the Akkerman area, are epigenetic minerals which commonly fill voids left by the decomposition of plant remains and commonly partly or completely replace organic matter. Cr-bearing smectites have also formed by decomposition of ultramafic and mafic rocks in the Ural Mountains, Brazil, Bulgaria, Italy, the Federal Republic of Germany, Norway, Yugoslavia, and Nevada. The chromian montmorillonite in the Cretaceous Hatrurim Formation, Israel (Gross *et al.*, 1967; Gross, 1977) was described as being of hydrothermal origin. Chromian montmorillonite was also found in this formation where it extends to the Daba marble area in west-central Jor-

dan (Khoury *et al.*, 1984). The chromian smectites and the chromian chlorites in sedimentary formations of the Colorado Plateau, such as in the Temple Mountain district, Utah (Hawley *et al.*, 1965, p. 100, Figure 35); the Thompson district, Utah (McConnell, 1954); the Slick Rock district, Colorado (D. R. Shawe, unpublished information); the Gartra prospect, Moffat County, Colorado (Cadigan, 1972); the Placerville area, Colorado (Bush *et al.*, 1959, p. 376); and the Rifle Creek area, Colorado (Botinelly, 1960, p. 23) are similar in occurrence. The chromian smectites and chlorites of the Colorado Plateau are found in uranium-vanadium deposits and are of epigenetic origin.

Table 1 summarizes the reported occurrences of volkonskoite and lists the likely identity of the species present, based on the chemical data presented in the cited work. A chronological summary of 20th century studies on volkonskoite and related Cr-bearing clays is given in Table 2, along with significant descriptions and/or results. Table 3 is a summary of selected chemical analyses from the literature of pure (either reported to be or interpreted by the present authors to be) volkonskoite and Cr-bearing members of the smectite group. Analyses 1, 2a, and 2b of volkonskoite (USNM R4820 and 16308) from the Okhansk area and analysis 20 of Cr-bearing beidellite (DRS-81-199) from Candalaria, Nevada, are new.

METHODS AND MATERIALS

Methods

All clay samples were examined using techniques described in Starkey *et al.* (1984). Major elements were determined by X-ray fluorescence spectroscopy using a Philips PW1600 simultaneous wavelength-dispersive spectrometer according to the method of Taggart *et al.* (1981). About 0.15 g of samples were fused with 8.0 g of lithium tetraborate by the methods of Taggart and Wahlberg (1980a, 1980b). Some elements were also verified by inductively coupled plasma and emission spectroscopic analyses. A Cambridge Stereoscan 250 Mk2 scanning electron microscope with an energy-dispersive X-ray analysis capability was used to examine samples at high magnification.

Thermogravimetric analyses were made on a Perkin-Elmer TGS-2 thermogravimetric analyzer at a heating rate of 4°C/min. Ferrous-ferric iron was determined by ⁵⁷Fe Mössbauer spectroscopy. Spectra were acquired at room temperature with a conventional constant acceleration system using a 10 mCi ⁵⁷Co : Rh source. The computer least-square fitting was aided by using Lorentzian line shapes and by assuming equal intensities and line widths for both lines of a quadrupole pair. The Fe²⁺ fraction was computed as the fractional integrated intensity of the Fe²⁺ resonance. Possible errors due to sample thickness and different recoilless frac-

Table 1. Reported occurrences and species designations of volkonskoite and other Cr-bearing smectites.¹

Location	Reported name	Species designation
Middle Kama River area, Perm Basin, U.S.S.R. (includes Okhansk area)	Volkonskoite. Kersten (1839), Kokscharov (1853), Angel (1913), Ivanova (1937), Aleksandrov <i>et al.</i> (1940), Borisenko and Borisenko (1962)	Volkonskoite
Uchtym and Udmurtia (formerly Vyatka), U.S.S.R.	Volkonskoite. Krotov (1902), Angel (1913), Kultyshev (1938)	Volkonskoite
Akkerman area, northern Ural Mountains, U.S.S.R.	Volkonskoite. Gudoshnikov <i>et al.</i> (1968)	Volkonskoite
Malka River area, northern Caucasus Mountains, U.S.S.R.	Chromian beidellite and beidellite. Serdiuchenko (1933, 1952)	Chromian montmorillonite
Rastiste, Yugoslavia	Chrome smectite (volkonskoite). Maksimović and Krstanović (1969)	Chromian smectite
Mottled zone, Nahal Ayalon and Hatrurim Formation, central Israel	Volkonskoite. Gross <i>et al.</i> (1967), Gross (1977)	Chromian montmorillonite
Daba area, central Jordan	Volkonskoite. Khoury <i>et al.</i> (1984)	Chromian montmorillonite
Mzongwe River, Mafungabusi, Zimbabwe	Volkonskoite. Anderson (1975)	Chromian nontronite?
Castiglione, Livorno, Italy	Volkonskoite. Sartori (1967)	Chromian montmorillonite
Groschlattengrün, Fichtelgebirge, Bavaria, Federal Republic of Germany	Volkonskoite. Weiss <i>et al.</i> (1954)	Chromian montmorillonite
Kurn, Bavaria, Federal Republic of Germany	Volkonskoite. Andritzsky (1963)	Chromian smectite
Nevrokop, Bulgaria	Volkonskoite. Dimitrov (1942)	Volkonskoite
Campo-Formo, Bahia, Brazil	Chromian nontronite and volkonskoite. Besnus <i>et al.</i> (1975)	Chromian nontronite
Froland, Arendal, Norway	Chromian montmorillonite (volkonskoite). Nilsson and Raade (1973)	Chromian smectite
Thompson, Utah	Volkonskoite. McConnell (1954)	Chromian smectite, and chromian chlorite
Temple Mountain district, Emery County, Utah	Chromium-bearing mica-clay. Hawley <i>et al.</i> (1965)	Chromian smectite(?)
Gartra prospect, Moffat County, Colorado	Chromium-bearing clays. Cadigan (1972)	Chromian chlorite and chromian smectite
Placerville, San Miguel County, Colorado	Chromium-bearing analogue of roscoelite(?). Bush <i>et al.</i> (1959)	Chromian chlorite and chromian smectite
Slick Rock district, San Miguel and Dolores Counties, Colorado	Chromium-bearing clay. Shawe (unpublished)	Chromian smectite(?) and/or chromian chlorite(?)
Rifle Creek area, Garfield County, Colorado	Chromium-bearing mica-montmorillonite and minor chlorite. Botinelly (1960)	Chromian smectite and chromian chlorite
Candelaria, Mineral County, Nevada	This paper	Chromian beidellite

¹ Assigned by the authors.

tions at the Fe³⁺ and Fe²⁺ crystallographic sites are included in the reported experimental uncertainties.

Cation-exchange studies were performed on 0.1434 g of sample R4820 and 0.2856 g of sample 16308 using 1 N ammonium chloride as the exchange solution. The matrix solution was 40 ml of 1 N NH₄Cl, 20 ml of methanol, and 40 ml of distilled water. Ca and Mg were determined by atomic absorption spectroscopy. Carbonate carbon (expressed as CO₂) was determined on 20 mg of sample 16308 by acid evolution of CO₂ and coulometric titration of the evolved CO₂ using a coulometric automatic titrator. Total carbon was determined on 147 and 154 mg of samples R4820 and 16308, respectively, using a Leco Cr-12 carbon-analyzer and combusting the samples at 1370°C in an O₂ atmosphere. The evolved CO₂ was determined by in-

frared methods. Organic carbon is expressed as the difference between total carbon and carbonate carbon.

Materials

A specimen (R4820) labelled "Wolchonskoite, Okhansk, Siberia, U.S.S.R." was obtained from the U.S. National Museum through the courtesy of John S. White, Jr. A second specimen (16308) labelled as being from the type locality was obtained later. It was labelled as "Nontronite (wolchonskoite), Mt. Efimiatsk, Urals, Siberia, U.S.S.R." Sample 16308 was obtained by the U.S. National Museum from the museum of the Mining School of St. Petersburg, Russia on March 17, 1884.

Both USNM samples of volkonskoite are 1- to 3-cm thick masses of dark to very dark, emerald-green (GSA

Table 2. Post-1900 chronological summary of studies on volkonskoite and other Cr-bearing smectites.

Year	Author(s)	Significant descriptions and/or results
1902	Krotov	Analysis from Uchtym, Vyatka, U.S.S.R.
1913	Angel	Two new analyses and role of water
1928	Pustovalov	Major summary for Perm Basin
1928	Kryzhanovski	Described deposits in Vyatka and Perm Governments
1933	Serdiuchenko	Five analyses of chrome-nonttronite from the Caucasus
1937	Ivanova	Analysis of volkonskoite from Mount Efimyata and shown to be related to montmorillonite
1938	Kultyshev	New deposits in Udmurtia; seven analyses of impure material
1940	Aleksandrov <i>et al.</i>	Summary of volkonskoite from the Perm Basin
1942	Dimitrov	First description of volkonskoite from outside the U.S.S.R. (Bulgaria)
1945	Ross and Hendricks	Summary of the montmorillonite group
1952	Serdiuchenko	Data on chromian montmorillonite and montmorillonite from Malka River area, Caucasus, U.S.S.R.
1952	Entsov <i>et al.</i>	Geology of Kama area volkonskoite deposits
1953	Davydov and Rechina	Synthesis studies of volkonskoite
1954	Weiss <i>et al.</i>	Chromian montmorillonite containing about 7 wt. % Cr ₂ O ₃ from Bavaria
1954	McConnell	Description of impure Cr-bearing smectite from Utah
1961	Ivanova	Differential thermal analysis data for volkonskoite and other smectites
1962	Borisenko and Borisenko	Analysis of volkonskoite from Samosadka, Kama River area
1963	Andritzky	Impure Cr-smectite with 6.7 wt. % Cr ₂ O ₃ from Bavaria
1966	Boldyrev and Mikheev	Infrared data for volkonskoite and other smectites
1966	Bentor and Gross	Chromian montmorillonite from Negev, Israel
1967	Sartori	Occurrence of chromian montmorillonite in Italy
1968	Gudoshnikov <i>et al.</i>	Volkonskoite and Cr-allophanoids from Akkerman area, U.S.S.R.
1969	Maksimović and Krstanić	Occurrence of chromian smectite in Yugoslavia
1969	Sanyal <i>et al.</i>	Studies on formation of synthetic Cr-bearing clays
1972	Petzold	Analysis of volkonskoite from the Urals, U.S.S.R.
1973	Nilssen and Raade	Chromian smectite with about 1% Cr ₂ O ₃ from Norway
1975	Besnus <i>et al.</i>	Chromian nontronite from Bahia, Brazil

Table 2. Continued.

Year	Author(s)	Significant descriptions and/or results
1975	Anderson	Cr-bearing nontronite from Southern Rhodesia (now Zimbabwe)
1977	Gross	Complete analysis of chromian montmorillonite from Negev; another from Hatrurim Formation
1978	Harder	Synthesis studies of clays including volkonskoite
1982	Heinbach and Rosch	Chromian montmorillonite from the "mottled zone," central Jordan
1984	Khoury <i>et al.</i>	Chromian montmorillonite from Jordan and one analysis of volkonskoite from the Okhansk area, U.S.S.R.
1984a	Mackenzie	Early history of the discovery of volkonskoite
1984b	Mackenzie	Constitution of and relationships among volkonskoites and chromian smectites
1985	Mackenzie	Discussion of volkonskoite and chromian montmorillonite from the Kama River area and Jordan for Soviet readers

Color Chart no. 5G 3/2), conchoidally fractured, homogeneous clay. Calcareous sandstone is attached to one surface of specimen R4820. Physical properties for the mineral are as given in the literature for volkonskoite (Ivanova, 1937; Aleksandrov *et al.*, 1940; Borisenko and Borisenko, 1962).

A sample (DRS-81-199) of a bright bluish-green clay associated with red to orange brown iron oxides and silicates was collected in 1981 by D. R. Shawe from the Lucky Hill pit, Candelaria mine, Mineral County, Nevada. The geology of the district was described by Page (1959). Serpentinite masses as large as 2000-m long and 100- to 400-m wide are exposed in the district. The serpentinite has been derived from ultramafic and mafic rocks. Deuteric and hydrothermal alteration has resulted in the formation of numerous gray-white and rusty, orange-brown areas. It is from one of these areas that the clay sample which contained minor amounts of quartz and kaolinite and <1-mm grains and relict grains of chromite was collected (Figure 1).

RESULTS

Okhansk region, Perm Basin, U.S.S.R.

A semiquantitative emission spectrographic analysis of specimen R4820 is given in Table 4. The major and minor element contents agree well with the results obtained (analysis 1, Table 3) by an X-ray fluorescence (XRF) analysis of 0.15 g of sample and an inductively coupled plasma analysis of 10.8 mg of sample. Two XRF analyses (analyses 2a and 2b, Table 3) of speci-

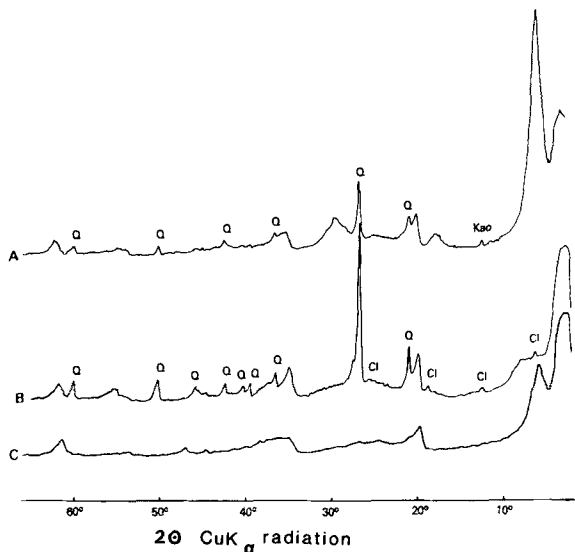


Figure 1. X-ray powder diffraction patterns for (A) chromian beidellite (DRS-81-199) from Candelaria, Nevada; (B) chromian montmorillonite from Thompson, Utah (USNM 107451); and (C) volkonskoite (USNM R4820) from Okhansk, U.S.S.R. Q = quartz; Kao = kaolinite; Cl = chlorite.

men 16308 are also listed in this table along with the average analysis (2c) used for calculation of the structural formula. Quantitative spectrographic analysis (Table 4) indicates the presence of 30 ppm Li. X-ray powder diffraction (XRD) studies of randomly oriented and oriented volkonskoite before and after glycolation and heat treatments (as per Starkey *et al.*, 1984) indicated no impurities (Figure 1). The XRD trace for sample R4820 is compared in Figure 1 with those for chromian beidellite from Candelaria, Nevada, and a sample of chromian smectite, quartz, and chromian chlorite from the Morrison Formation near Thompson, Utah (U.S. National Museum specimen 107451). Cell refinement was attempted for both the Okhansk and Candelaria samples, but because of the broadened peak widths and the low number of reflections, the refinements were not convergent. Thermogravimetric analyses (TGA) of volkonskoite and the Candelaria chromian beidellite are similar (Figure 2). Loss-on-ignition (LOI) values determined on portions of the sample fractions of R4820 and 16308 used for XRF analyses are greater than the values for total water obtained by coulometric moisture analysis (Table 3). The differences are due to the amount of contained organic and carbonate carbon. The XRF analyses of R4820 and 16308 are similar to each other and to other volkonskoites from the Kama area red beds (Table 3). Scanning electron microscope (SEM) examination with energy-dispersive system (EDS) capability showed no other chemically different minerals to be present.

Heller-Kallai and Rozenson (1981) described the use of Mössbauer spectroscopy to determine the valence

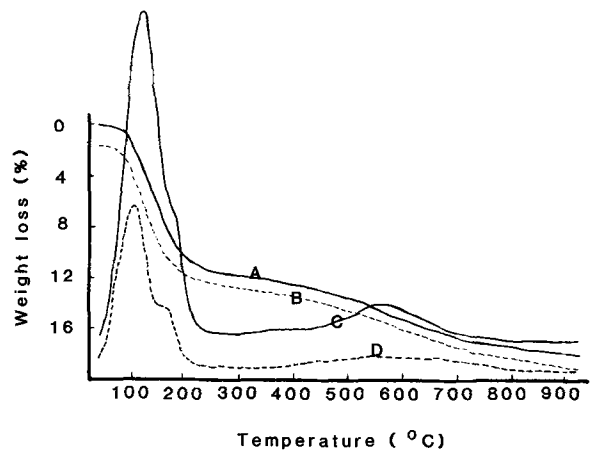


Figure 2. Thermogravimetric analysis weight loss and first derivative curves for (A, C) volkonskoite (USNM R4820) from Okhansk, U.S.S.R.; and (B, D) chromian beidellite (DRS-81-199) from Candelaria, Nevada.

state of iron in clays. Using this method on a volkonskoite from an unspecified locality, they found that all the contained iron was in the ferric state. Mössbauer data for samples R4820 and 16308 (determined by D. L. Williamson, Colorado School of Mines, Golden, Colorado) indicated that nearly all of the iron in these samples is ferric also (Figure 3). Ferrous iron comprised $2 \pm 1\%$ of the iron in R4820 and $9 \pm 3\%$ of the iron in sample 16308. The chemical analyses (analyses 1 and 2, Table 3) for iron were consequently partitioned on the basis of the Mössbauer data. Both of the stron-

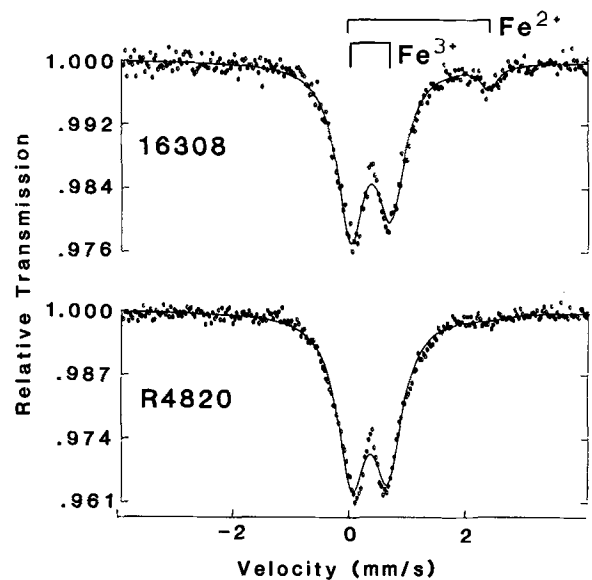


Figure 3. Room-temperature ^{57}Fe Mössbauer spectra of volkonskoite samples. Solid line is least-squares computer fit of sum of three Lorentzian lines. Lower velocity Fe^{2+} line is unresolved from Fe^{3+} .

Table 3. Continued.

	12	13	14	15	16	17	18	19	20	21
	Volkonskoite, Neurokop, (Lyazvevo) Bulgaria, Dimitrov (1942)	Chromian montmoril- lonite, Daba area, Jordan, Khoury <i>et al.</i> (1984) 1c	Chromian nontronite, Bahia, Brazil, Sample "C," Besnus <i>et al.</i> (1975)	Chromian nontronite, Bahia, Brazil, Sample "D," Besnus <i>et al.</i> (1975)	Chromian montmoril- lonite, Malka River Cauca- sus Moun- tains, U.S.S.R., Serdyyuchen- ko (1952)	Chromian montmoril- lonite, Ha- shal Ayalon, Israel, sam- ple #131, Gross (1977)	Chromian montmoril- lonite, Hatru- rim Forma- tion, Israel, sample #157, Gross (1977)	Chromian montmoril- lonite, Casti- glioncello, Ita- ly, Sartori (1967)	Chromian beidellite, Candelaria, Nevada, DRS-81- 199	Chromian beidellite, Candelaria, Nevada, DRS-81- 199
Cr ₂ O ₃	15.02	16.05	11.0	3.2	5.02	7.68	6.67	1.14	5.62	6.39
SiO ₂	45.70	42.27	49.3	45.2	43.14	45.08	46.24	46.35	54.3	51.06
Al ₂ O ₃	4.85	2.95	9.6	7.9	16.07	10.18	12.87	15.87	16.9	17.85
MgO	0.58	9.69	4.47	3.52	3.45	5.37	5.20	6.55	2.14	2.43
CaO	3.10	2.88	0.2	<0.2	1.46	2.45	2.33	Traces	1.93	2.19
Fe ₂ O ₃	6.36	None	15.2	30.7	4.70	1.86	2.26	2.20	1.61	1.83
FeO	—	None	—	—	0.61	—	—	—	—	—
TiO ₂	N.D.	None	0.16	0.20	0.96	0.33	0.37	0.45	0.16	0.18
V ₂ O ₅	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
MnO	N.D.	None	0.08 ³	0.15 ³	0.21	N.D.	N.D.	N.D.	<0.05	<0.05
K ₂ O	N.D.	0.03	<0.05	<0.05	N.D.	0.03	0.01	0.24	0.1	0.13
Na ₂ O	N.D.	None	<0.05	<0.05	N.D.	0.12	0.08	0.92	<0.05	<0.05
P ₂ O ₅	N.D.	N.D.	0.10	0.07	0.01	0.64	0.45	N.D.	<0.05	<0.05
SO ₃	N.D.	N.D.	N.D.	N.D.	0.15	0.39	0.08	N.D.	N.D.	N.D.
NiO	0.54	N.D.	0.80	1.4	0.30	N.D.	N.D.	Traces	N.D.	N.D.
CoO	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
C _{org}	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
LOI (920°C)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
H ₂ O+	7.37	25.25	8.1	7.72	7.34	7.21	10.12	12.10	17 ⁵	17.13
H ₂ O—	16.38	—	(14.0)	(13.6)	16.66	16.97	14.67	14.70	15.34 ¹	—
Total	99.90	99.12	99.01 ⁴	100.06 ⁴	100.08	98.31	101.35	100.52	98.11 ⁶	99.19 ⁷

N.D. = not determined.

¹ Carl Fisher microcoulometric moisture analysis; water determined as total water. ² Determined at about 160°C. ³ Mn₂O₄. ⁴ Sample dried at 110°C. ⁵ Determined by thermal gravimetric analysis (900°C). ⁶ Uncorrected analysis. ⁷ Corrected for 8% admixed quartz and 3% admixed kaolinite. ⁸ Includes 0.15 wt. % CO₂ (carbonate carbon). ⁹ Determined from Mössbauer spectroscopy. ¹⁰ Average of 5 analyses (Table 7). ¹¹ Average of 10 analyses (Table 7). ¹² 2c is average of 2a and 2b.

Table 4. Six-step semiquantitative emission spectrographic analyses of volkonskoite from Okhansk, U.S.S.R., and chromian beidellite from Candelaria, Nevada.

Element	Volkonskoite (pure) (USNM R4820)	Chromian beidellite (includes an estimated 3% kaolinite and 8% quartz) ¹ (DRS-81-199)
Fe	3%	1.5%
Mg	3%	1.0%
Ca	1.5%	0.7%
Ti	0.015%	0.1%
Si	major	major
Al	3.0%	7.0%
Na	0.07%	0.1%
K	N	N
P	N	N
Mn	500 ppm	150 ppm
Ag	3	1.5
B	70	30
Ba	300	70
Be	3	1
Co	70	5
Cr	major	3.0%
Cu	300	50
Ni	150	700
Pb	N	300
Sb	N	150
Sc	200	30
Sn	N	30
Sr	70	150
V	300	300
Y	50	N
Zn	N	1500
Zr	100	30
Ga	30	30
Yb	3	N
Li	30	N.D.
Rb	N10	N.D.
Cs	N10	N.D.

Rare alkalis (Li, Rb, Cs) determined by quantitative emission spectrography (N. M. Conklin, U.S. Geological Survey, Denver, Colorado, analyst). N.D. = not determined; N = not detected at respective limit of detection.

¹ Determined by X-ray powder diffraction.

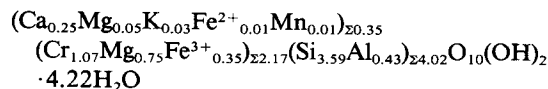
gest lines (labeled Fe³⁺) in Figure 3 are broad, which indicates that they are due to the presence of M(1) and M(2) octahedral Fe³⁺ iron sites.

Results obtained from cation-exchange studies of samples R4820 and 16308 were: CaO, 2.94% and MgO, 0.35%, and CaO, 1.23%, MgO, 0.88%, respectively. Thus, for both samples most or all of the Ca is in the exchangeable interlayer position and essentially all of the Mg is in the octahedral sheet of the 2:1 layer. Na and K were looked for but not determined because of the small amounts present.

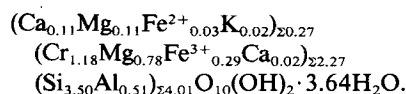
Structural formulae for the two analyzed volkonskoites were calculated from analyses 1 and 2c (Table 3) on the basis of 11 oxygen equivalents. The tetra-

hedral sheet was filled by the Si and Al. All the chromium and ferric iron was placed in the octahedral sheet together with nonexchangeable Ca and Mg. The ferrous iron was considered as exchangeable. A site occupancy of 2.20 for the octahedral sheet was obtained for the average of the five volkonskoite analyses given by Mackenzie (1984b). This occupancy compares favorably with the calculated formulae for samples R4820 and 16308 shown below:

R4820



16308

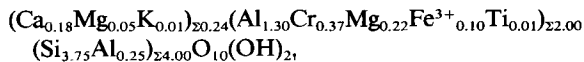


The data presented by Khoury *et al.* (1984) for the Jordanian Fe-free volkonskoite were interpreted by those authors to indicate a 'di-trioctahedral' structure. One problem does exist with both volkonskoite specimens analyzed in the present paper: regardless of how the structural formulas are calculated, the tetrahedral site is partially vacant. Because of structural constraints, vacancies in the tetrahedral sheet should not exist, and small amounts of a noncrystalline or poorly crystalline chromium oxide-hydroxide, such as CrO(OH) and/or organic carbon-bearing chromium alophanoids, are likely present. Chromium is not known in tetrahedral coordination in any layer silicate, and noncrystalline or poorly crystalline Fe and V oxide-hydroxide analogues are known (i.e., FeO(OH) and VO(OH)). Because the tetrahedral sheet in both USNM samples is completely filled with Si and Al, and nonexchangeable Ca and/or Mg are in the octahedral sheet together with most of the determined Cr, an excess of 9% CrO(OH) by weight exists in sample R4820 and 3% in sample 16308. The excess Cr cannot be added into the octahedral sheet because of charge balance constraints.

Volkonskoite from near the village of Efimyata was described as having a fibrous texture (Ivanova, 1937), and Kultyshev (1938) described the volkonskoite from Urdmurtia as being fibrous in habit as well. The volkonskoite from near Efimyata, however, was noted to contain minute dark grains which upon heating transformed into small, green hexagonal flakes of what was probably Cr₂O₃ (Ivanova, 1937). Dehydration of CrO(OH) would result in the formation of the anhydrous oxide. The small amount and probable noncrystalline character of the CrO(OH) would have precluded its detection by X-ray powder diffraction. Gudoshnikov *et al.* (1968) described volkonskoite and

associated colloidal, organic carbon-bearing chromium allophanoids from the Akkerman area in the U.S.S.R.

A semiquantitative emission spectrographic analysis of the bluish-green clay from the Candelaria district is given in Table 4. Material that was purified as much as possible but still contained minor quartz and kaolinite (Figure 1) was analyzed by XRF methods (analysis 20, Table 3). A calculated structural formula based on the analysis and corrected for admixed quartz and kaolinite (analysis 21, Table 3) is listed below, based on 11 oxygen atoms:



This formula is that of a chromian beidellite.

DISCUSSION

An examination of the literature (summarized in Tables 1 and 2) shows that the mineral name volkonskoite has been applied to smectites containing from 1 to 30 wt. % Cr_2O_3 . As stated by Brindley (1980), the name volkonskoite should be restricted to a chromium-bearing dioctahedral smectite, in which chromium is the dominant octahedral site cation.

On the basis of electron microprobe studies, Khoury *et al.* (1984) stated that a volkonskoite from the type area near Okhansk is a mixture of at least three smectite phases. Our examination shows the presence of compositionally zoned single-phase material. Aleksandrov *et al.* (1940) concluded on the basis of optical and DTA data that volkonskoite was a heterogeneous mixture composed of "amorphous" silica, kaolin, and adsorbed alkaline earth elements. On the basis of available chemical analyses, Ross (1960) concluded that volkonskoite was a valid species because Cr was the dominant cation. Gudoshnikov *et al.* (1968) described in detail the existence of volkonskoite and Cr-allophanoids together in the sedimentary environment. Their calculated structural formulae for volkonskoites from the Akkerman area and the Perm Basin show large amounts of chromium in the tetrahedral sheet as well as the octahedral sheet, which is unlikely.

The ten analyses of volkonskoite from the Perm Basin (Table 3) are remarkably similar to one another. These samples and many others for which analyses have been published are from an area of about 2500 km² in the Perm Basin (Entsov *et al.*, 1952). If these samples, which are also chemically similar to one from Jordan described by Khoury *et al.* (1984), represent mixtures of three or more different smectites and non-crystalline colloids, they are the result of a set of extraordinarily uniform depositional and geochemical conditions over a large area within the basin. The ten analyses given in Table 3 are stated or interpreted to be of 'homogeneous-appearing' material. Incomplete or obviously impure analyses were not included.

Besnus *et al.* (1975) interpreted the 'chromiferous' nontronites from Bahia, Brazil, to be a continuous solid solution series between volkonskoite and nontronite, in which chromium and iron substitute for one another in the octahedral position. The Mössbauer data of Heller-Kallai and Rozenson (1981) and those from this paper support this hypothesis.

CONCLUSIONS

Despite numerous studies, some of which were detailed, dating from 1830, volkonskoites from the Perm Basin as well as from other areas still require additional detailed investigation to resolve completely (1) whether they are monominerallic or mixtures of different smectites and/or possible noncrystalline substances (Khoury *et al.*, 1984); and (2) whether reports of chemical variations in single samples are due to compositional zonation of a single smectite phase. The latter possibility has not been conclusively shown; however, the mineral which we examined appears to be a valid species, inasmuch as it is a single compositionally zoned smectite. Chemical analyses show major Cr (>20 wt. % Cr_2O_3) and also a relatively narrow range of individual oxide values as well as bulk compositions. Chromium is the dominant cation in the octahedral sheet. XRD and SEM examination suggest that only one mineral is present. Therefore, the mineral should be defined as recommended by Brindley (1980) as a dioctahedral member of the smectite group containing dominant chromium in the octahedral position. Varieties between end-member compositions should be described by chemical element adjectives (Bayliss, 1975), e.g., chromian montmorillonite or chromian nontronite.

True volkonskoite is known only from the U.S.S.R. and Bulgaria. The chromium montmorillonite from Jordan (Khoury *et al.*, 1984) is very close to being a volkonskoite, but nevertheless should be described as a chromian montmorillonite.

Following the recommendation of the Committee on New Minerals and New Mineral Names, I.M.A., sample 16308 is established as a neotype and sample R4820 as a cotype.

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