AN AMERICAN OCCURRENCE OF VOLKONSKOITE

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ABSTRACT

Chromium-bearing members of the montmorillonite group have been reported heretofore only for Russian localities, where they have been related genetically to serpentines. A green mineral which occurs in high-angle fissures in the Morrison formation (Upper Jurassic) near Thompsons, Utah, contains about 2 percent Cr_2O_3. Data were obtained by optical and electron microscopy, x-ray powder diffraction, and gravimetric and spectroscopic chemical methods. The ultimate source of the chromium remains an unresolved geochemical question, as do the sources of vanadium and uranium in the Morrison sandstone.

INTRODUCTION

For about three decades Professor D. J. Demorest of the Department of Metallurgy, The Ohio State University, has been interested in producing and prospecting for uranium ores near Thompsons, Utah. He had noticed on numerous occasions a bright-green discoloration on certain exposed surfaces of the Morrison formation and was aware that samples containing this green substance contained significant quantities of chromium.

During one of his recent sojourns in Utah, Professor Demorest collected several pounds of the sandstone which showed prominent amounts of the green constituent. He requested that the writer examine this material in order to determine its mineralogical characteristics.

Preliminary examination with the petrographic microscope indicated a moderate birefringence and microcrystalline character, which suggested that it was a clay of the montmorillonite type. A powder diffraction pattern confirmed this tentative conclusion. However, it remained necessary to justify the supposition that this clay mineral was the essential chromium-bearing constituent, inasmuch as Professor Demorest had made all of his preliminary analyses for chromium on highly impure samples. Furthermore it seemed desirable, in light of the rarity of such chromium-bearing clays, to determine some of its properties. Except for the brief statement by Ross and Hendricks (1945) that material from the type locality produced a typical nontronite pattern, no new data on volkonskoite have been presented during the past two decades.

The measurements described herein involved the cooperation of several of my colleagues, as will be indicated. Mr. John H. Melvin, Chief of the

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Division of Geological Survey, Ohio Department of Natural Resources, granted permission to include an examination of this clay as a segment of a more general study of clays and shales which is being undertaken under the auspices of the Division of Geological Survey with the aid of equipment made available by a grant from the Edward Orton Junior Ceramic Foundation.

EXPERIMENTAL DATA AND CONCLUSIONS

It was not feasible to separate adequate pure material for chemical analysis by gravimetric methods because of the complexity of the mineral composition of the Morrison sandstone. Consequently a complete chemical analysis would not have value commensurate with the skill and labor necessary to obtain it.

Using a gram of the finer of two samples separated by water elutriation, Professor Demorest determined the constituents indicated in Table 1. Here comparisons with analyses for Russian materials (Serdiuchenko, 1933) are shown. Although the material under consideration contains far less Cr_2O_3 than the material to which the name, volkonskoite, was originally applied, the term seems to be appropriate for any montmorillonite-type clay containing a significant amount of chromium.

Spectroscopic determinations, made by Mr. E. D. Loughran under the direction of Professor J. I. Watters, furnished information on additional constituents (Table 1), but were of further value in determining the approximate purity of the sample analyzed by Professor Demorest. Using the method of Harvey (1947), five different samples were analyzed spectroscopically. From these results it was concluded that the sample analyzed by Professor Demorest contained merely 80-85 percent of the chromium-bearing clay. The contaminating substances were essentially quartz, a muscovite-like mica, and a dark-colored substance.

This dark-colored substance, which is occasionally glossy black by reflected light and dark brown or opaque (depending upon thickness) by transmitted light under the microscope, is intimately admixed with many flakes of the green material. Inasmuch as the diffraction pattern of selected dark-colored material was essentially indistinguishable from selected flakes of the green mineral, it is concluded that the black substance has no discernable diffraction pattern under the experimental conditions, and represents carbonized organic matter.

It was surmised that the vanadium content might be associated with this organic material because of the common association of vanadium with organic matter in the Morrison formation. However, it was not possible to confirm this supposition by spectroscopic analysis inasmuch as the V:Cr ratio did not appear to increase for the dark-colored sample when compared with the selected green flakes. Thus the question of whether or not the clay mineral contains most, or all, of the V_2O_5 remains obscure. It is concluded, however, that the pure clay mineral contains 2 percent or more

TABLE 1. — ANALYSES OF CHROMIUM-BEARING CLAYS OF THE MONTMORILLONITE TYPE

	I	II	III	IV	V	VI
SiO_2	n.d.	46.09	36.69	43.14	45.83	44.47
Al_2O_3	19.70[g]	24.04	16.77	16.07	18.55	19.63
Fe_2O_3	3.10[g]	3.96	8.70	4.70	9.29	10.85
Cr_2O_3	1.67[g]	1.12	3.76	5.02	0.74	1.02
FeO	*	0.33	7.83	0.61	0.71	0.47
MnO	0.21[w]	0.49	none	0.21	tr.	tr.
NiO	0.02[w]	tr.	none	0.30	0.09	0.10
MgO	3.72[g]	6.99	1.60	3.45	2.12	1.86
CaO	0.23[g]	1.86	2.57	1.46	1.69	1.50
TiO_2	0.45[g]	1.04	—	0.96	0.22	0.20
H_2O^+	n.d.	7.26	12.90	7.32 }	20.20	20.00
H_2O^-	n.d.	5.67	8.42	16.66 }		
Others	**	—	—	0.16	0.63	0.29

I—Impure material from near Thompsons, Utah. [g] Determinations by D. J. Demorest. [w] Determinations by J. I. Watters and E. D. Loughran. * Included with Fe_2O_3 which is total iron. ** V_2O_5[g] 0.32, Ignition loss ca. 13.5 percent.

II—From upper course of the Great Laba River (Serdiuchenko, 1933).

III—From the Gedmyshkh Valley (Idem.)

IV—From below ore bed in the Cheghet-Lakhran Valley (Idem.); others: P = 0.01, S = 0.15.

V—Emerald mines, Ural Mountains (Idem.); others: K_2O = 0.31, Na_2O = 0.32.

VI—Same as V but on washed material (Idem.); others: K_2O = 0.15, Na_2O = 0.14.

of Cr_2O_3 and that no other mineral is present which contains a significant quantity of chromium.

Electron micrographs, prepared by Professor A. F. Prebus, indicate the fibrous nature of the volkonskoite but also indicate contamination by a muscovite-like mica (Pl. 1A). In Plate 1B the fibers are sufficiently dispersed to avoid high opacity due to aggregation of fibers.

Although a diffraction pattern was obtained from a microscopically selected sample of green polycrystalline flakes, and it exhibited merely lines of a member of the montmorillonite group, the excellence of resolution was somewhat better for the pattern obtained from material which remained in suspension for more than 72 hours (Table 2). This pattern indicates the presence of very fine-grained quartz and a muscovite-like mica. The unit-cell dimensions taken from these data are: $a_0 = 5.17$ and $b_0 = 9.00$, both ± 0.05 A. Under the prevailing experimental conditions $c_0 = 12.91 \pm 0.05$ A.

Powder diffraction patterns, prepared with filtered chromium and/or iron radiation, were available for several other members of the montmorillonite group. According to increasing a_0 - b_0 dimensions their order is as follows: montmorillonite (near Montmorillon, France), volkonskoite (Utah), nontronite (near Garfield, Wash. A.P.I. no. 33), saponite

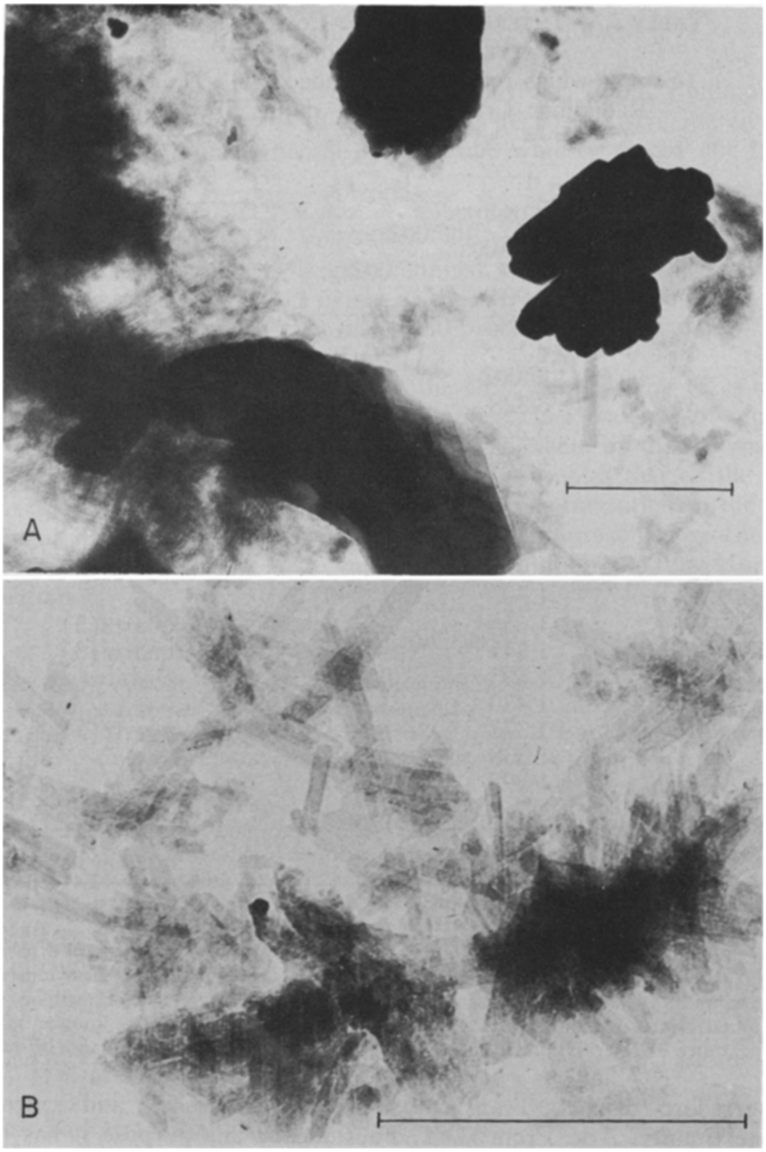

PLATE 1. — Electron micrographs of (A) volkonskoite showing contamination by micaceous mineral (Magnification 25,000 X); (B) dispersed fibers of volkonskoite. (Magnification 55,000 X.).

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TABLE 2. — INTERPRETATION OF POWDER DIFFRACTION PATTERN OF VOLKONSKOITE
(Sample which remained suspended for >72 hours.)
Radiation: CrKα. Camera radius 57.3 mm.

Line No.	I[1]	d	Indices	Remarks[2]
1	>10(b)	{17.98 / 9.56}	001	+ mica(s)
2	½	6.59	002	
3	<½	4.904	—	mica(s)
4	3	4.452	110, 020(?)	
5	1	4.197	—	quartz(7)
6	½	3.490	—	mica(m)
7	3	3.328	—	quartz(10) + mica(vs)
8	1	3.228	004	
9	5(b)	2.570	130, 200, 005	+ mica(vs)
10	1	2.399	—	mica(m)
11	½	2.242	220, 040(?)	
12	½	2.151	006	+ mica(s)
13	½	1.979	—	mica(vs) + quartz(2)
14	½	1.703	150, 240	
15	½	1.666	—	quartz(3)
16	1	1.541	—	quartz(3)
17	6	1.503	060	+ mica(s)
18	1	1.480	330	
19	1	1.372	—	quartz(7)
20	½	1.338	—	(?)
21	2(b)	1.299	260, 400	
22	½	{1.264	350, 170, 420	+ quartz(2)
23	1(b)	1.251}		
24	½	1.229	—	quartz(1)

[1] Estimated relative intensities. (b) indicates a band, which in the first case is continuous between the limits given.
[2] The relative intensities of quartz lines are indicated in parentheses on the basis of 10 for the strongest line of the quartz pattern. Relative intensities for muscovite (Nagelschmidt, 1937) are indicated as very strong (vs), strong (s) or medium (m). The mutual intensity relationships volkonskoite: quartz: mica are not known, so that the appearance of a weak quartz line does not necessarily imply an abundance of quartz.

(Krugersdorp district, Transvaal. From H. Heystek), and sauconite (Boone County, Ark. From G. T. Faust). For this purpose it has been assumed that $b_0 = a_0\sqrt{3}$; *i.e.*, no attempt was made to determine a_0 and b_0 independently.

OCCURRENCE

The Morrison formation of Upper Jurassic age contains numerous fossil remains (Stokes, 1952). Replacements involving trees and teeth and bones may comprise valuable sources of carnotite in this vicinity.

Whether or not the black substance of organic origin which is associated with the volkonskoite contains vanadium, it displays little evidence of radioactivity. The greatest activity measured by Mr. C. M. Phillippi was obtained for about 3 grams of elutriated material; it gave merely 0.15 c.p.s. above background with the Geiger tube window placed one-fourth inch above the sample.

The Morrison sandstone contains numerous mineral constituents, including glass shards. The volkonskoite is not uniformly distributed throughout the rock but is largely confined to fractures which cut the strata at high angles. Thus the origin of the clay mineral is supposed to be related to circulation of ground waters and probably also to the occurrence of volcanic ash in the formation.

Serdiuchenko (1933) supposes that the chromium-bearing clays which he studied are related in origin to serpentines. The material of analysis II (Table 1) is from coal-bearing Jurassic sediments of the Gedmyshkh Valley. Although this occurrence most nearly resembles that of the Utah material, serpentines do not underlie the Morrison formation in the area.

The ultimate source of the chromium remains an unresolved geochemical question, as do the sources of vanadium and uranium in the Morrison formation.

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