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HIGH-POTASSIUM CRYPTOMELANE FROM TARAPACA PROVINCE, CHILE

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ABSTRACT

Cryptomelane from a vein in the Province of Tarapaca, Chile, contains 6.6 percent K_2O, higher than any cryptomelane previously recorded.

INTRODUCTION

During recent years, several reports on the manganese deposits of Chile have appeared (Biese, 1956; Ruiz, 1965). In each, there is a description of some deposits of uncommon type near Estacion Coronel Alcerreca, in the Province of Tarapaca, Department of Arica. In view of the uncommon nature of the deposits, it seemed desirable to examine the contained minerals closely. Through the courtesy of a mutual friend, George E. Ericksen of the U.S. Geological Survey, one of us (RSO) collected a suite of specimens of the manganese minerals and associated rocks in the area, and these have been examined by D. F. Hewett.

A semiquantitative spectrographic analysis of vein material indicated a potassium content of 7.0 percent, much higher than previously recorded for cryptomelane; this was confirmed by chemical analysis. The features of the deposits are described briefly.

GEOLOGIC FEATURES

In the altiplano of the Province of Tarapaca, northern Chile, at an elevation of about 4,000 meters, beds of manganese oxide crop out in a large area drained by the Lluta River. The area lies about 90 kilometers northeast of Arica, near Estacion Coronel Alcerreca on the Arica-La Paz Railway. Within the area, in the sediments of the Huaylas Formation, which is probably Pleistocene in age, the following three members have been recognized (Ruiz, 1965):

Uppermost member: thickness about 60 meters. This member is composed largely of ignimbrites, rhyolitic tuffs, and tuffites with intercalated thin layers of conglomerate and sandstone, and contains beds of nearly pure manganese oxides that range in thickness from 1 to 5 meters and seem to extend along the strike as much as 4 kilometers. Other beds of sandstone are impregnated with manganese oxides. Samples 280 and 281 (Table 1) were collected from one of the beds of nearly pure manganese oxides.

TABLE 1. SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSES MANGANESE OXIDES FROM VEIN AND BED ALCERRECA, PROVINCE OF TARAPACA, CHILE[a]

Field No.	Alcerreca 3 Vein	Alcerreca 4 Bed	Alcerreca 5 Bed
	279	280	281
Si	0.5	0.7	M
Al	0.3	0.3	0.2
Fe	0.05	0.15	0.07
Mg	0.015	0.07	0.015
Ca	0.2	0.5	0.2
Na	0.2	0.5	0.15
Na (chemical)	0.067	0	0
K	7.0	7.0	2.0
K (chemical)	5.4	0	0
Ti	0.003	0.01	0.001
Mn	M	M	M
Ag	0	0	0.0002
As	1.5	0.1	1.5
B	0	0	0.003
Ba	0.003	5.0	0.01
Be	0.0007	0.0003	0.0003
Co	0.005	0.07	0.01
Cr	0.0015	0.00015	0.002
Cu	0.005	0.05	0.05
Mo	0.07	0.03	0.005
Ni	0.0015	0.007	0.002
Sr	0.07	0.5	0.05
Tl	0.01	0.03	0.007
V	0.15	0.1	0.005
Y	0	0.003	0
Yb	0.0003	0.0005	0
Zn	0.5	0.02	0.3
Zn (Chemical)	0.58	0	0

Looked for but not detected: P, Au, Bi, Cd, Ce, Ga, Ge, Hf, Hg, In, La, Li, Nb, Pb, Pd, Pt, Re, Sb, Sn, Ta, Te, Th, U, W, and Eu.

[a] Chris Heropoulos, analyst.

Middle member: thickness about 80 meters. This member is made up largely of beds of white to yellowish-red sandstone and clay. There are minor intercalations of white clay and diatomite. No beds of manganese oxides have been observed in this member, but there are sporadic small veins of pure manganese oxides. Sample 279 was collected from a vein of manganese oxide (crytpomelane) about 4 centimeters thick.

Lowermost member: thickness about 120 meters. This member is largely conglomerate composed of rounded and subangular pebbles of andesite and rhyolite in a sandy matrix. No beds of manganese oxide have been observed in this member.

It seems significant that, in the area examined, beds of low- and high-grade manganese oxides have been found only in the uppermost member of the Huaylas Formation, but veins of pure manganese oxide as much as 10 centimeters thick have been found in the middle member and the lower part of the uppermost member, but below the beds of manganese oxide. Thus far, no vein of oxides is connected with a bed of oxides so their relation cannot be proven. The chemical features of the oxides in the vein and the bed, however, such as the high content of potassium and arsenic as well as the absence of veins in the sedimentary section above the beds of manganese oxides in the uppermost member, favor the idea that the fractures that contain the veins were the source of the manganese in the beds.

MINERALOGY

Early in the study of the specimens from this area, spectrographic analyses showed that the principal mineral of both the vein and the bed is cryptomelane but that the content of potassium is higher than ever recorded for the mineral. Later, a chemical analysis showed that the potash content is 6.6 percent whereas the range in seven analyses of specimens from the United States is from 3.10 to 3.92 percent (Richmond and Fleischer, 1942). The possible relation of the veins of the area to the beds, is an intriguing problem.

Crytomelane is the only oxide recognized in the vein, and it is the principal oxide in two specimens from the bed of the purest material. The specimen from the vein in the middle member is made up of alternating layers of hard black and softer brown oxides (No. 279), and, as the layers outward from each wall match closely, it seems that the layers were deposited outward from the walls in an open fissure. X-ray diffraction analyses of the hard black and soft-brown oxides are identical and indicate that both are cryptomelane.

Table 1 shows one spectrographic analysis of the vein oxide (No. 279) and analyses of two specimens of layers in the bed (Nos. 280 and 281). X-ray diffraction analyses show that sample No. 280 is largely cryptomelane with some psilomelane, whereas sample No. 281 is hard-black pure cryptomelane, slightly vesicular, resembling some varieties of lava. Both the spectrographic analyses of the three specimens and the chemical analysis of No. 279 show noteworthy amounts of arsenic and zinc; thallium is present in the three specimens. Small amounts of arsenic and thallium are persistently present in oxides of hypogene origin and much less frequently in the oxides of supergene origin (Hewett, Fleischer, and

Conklin, 1963). The absence of tungsten in both the vein and bedded oxides is worthy of note. The Uncia locality in Bolivia, where Lindgren (1922) found that manganese oxides deposited by an active hot spring contained 2.19 percent tungsten, lies about 200 miles west of Alcerreca.

R. C. Erd of the U.S. Geological Survey has been kind enough to review the chemical data and makes the following comment concerning the formula of cryptomelane:

“The composition of cryptomelane was first given by Fleischer and Richmond (1943) as KR_8O_{16} ($R = Mn^{4+}$ chiefly, also Mn^{2+}, Zn, Co). Later work by Bystrom and Bystrom (1950) on the crystal structure of the related barium mineral hollandite showed that there were two positions that could be filled by K (or Ba) ions, and the formula of cryptomelane has been given in various modifications of a formula close to $K_{2-y}Mn_{8-x}O_{16}$ in the simplest terms (Gruner, 1943; Mathieson and Wadsley, 1950; Hey, 1955, p. 37; Ramdohr and Frenzel, 1956, p. 21, 54; Berry and Thompson, 1962, p. 203; Strunz, 1966, p. 183). There is some variation, due largely to variations in the state of oxidation of Mn. Water has been rejected in the calculation of the formula given in Table 2 in order that the data may be compared directly with those given by Gruner (1943, Table 3, p. 502).”

TABLE 2. CHEMICAL ANALYSIS OF CRYPTOMELANE FROM A VEIN AT TARAPACA, CHILE[a]

Oxide	Weight percent	Ion	Ions/Formula[b]	
MnO_2	82.4	Mn^{+4}	7.271	7.36
As_2O_5[c]	1.28	As^{+5}	0.085	
ZnO	0.73	Zn^{+2}	0.069	0.70
MnO	5.8	Mn^{+2}	0.627	
Na_2O	0.09	Na^{+1}	0.022	1.10
K_2O	6.6	K^{+1}	1.075	
H_2O^{+}[d]	1.60			
H_2O^{-}[d]	0.24			
Total	98.74			

[a] Lois B. Schlocker, analyst.

[b] Ions per formula were calculated following a procedure described by Jackson *et al.* (1967) and using the IBM System 360-Model 65 computer: normalizing factor = 7.6712, weight percentage of oxygen = 33.3703, formula = $Na_{0.02}\,K_{1.07}\,Mn_{0.63}\,Zn_{0.07}\,Mn_{7.27}\,As_{0.08}\,O_{16}$, density = 4.40_3 $_{gcm}$-3 (calculated for this composition).

[c] Reported as $As_2O_3 = 1.1$ weight percent.

[d] Rejected from calculations (*see* discussion in text).

Within the section of sedimentary rocks, not far from the bed of manganese oxides, layers of diatomaceous earth have been sporadically altered to dense gray opal within which there are scattered cylindrical cavities, probably once occupied by plant remains.

In Table 3 are assembled analyses of the alkalies and barium in samples of cryptomelane that have been identified by X-ray study. It will be noted that the atomic sum (K+Na+Ba+Sr+Ca) is generally less than, but near to 1, the maximum being 1.28 for material from Sitapar, India; similar calculations for hollandite (Fleischer, 1964) show a maximum of 1.18. Attention is called to the remarkably low alkali content of material from Sandur, India (Naganna, 1964), which gave the normal X-ray pattern of cryptomelane.

TABLE 3. ANALYSES OF ALKALIES AND BARIUM IN SAMPLES OF CRYPTOMELANE

Locality	Weight per cent			ΣK+Na+Ba +Sr+Ca (O=16)	Mode of Origin	Authority
	K_2O	Na_2O	BaO			
Arizona, Tombstone	3.50	0.44	0.13	0.69	Supergene	Richmond and Fleischer (1942)
Arkansas, Sugar Stick	3.84	0.56	trace	0.76	do	do
Colorado, Silver Cliff	3.46	0.81	—	—	do	Hewett and Fleischer (1960)
Montana, Phillipsburg	3.10	0.48	0	0.62	do	Richmond and Fleischer (1942)
New Mexico, Luna mine	3.88	0.47	1.04	0.79	Hypogene	Hewett and Fleischer (1960)
Tennessee, Neely mine	4.04	0.66	0.77	0.86	Supergene	Hewett and Fleischer (1960)
Brazil, Merida mine	3.92	0.20	—	—	Supergene	Horen (1953)
Chile, Tarapaca	6.6	0.09	0.003	1.10	Hypogene	Hewett and Salas (1968)
Gawari Warhona, India[a]	6.06	0.97	4.06	—	?	Fleischer (1964)
Sitapar, India	5.95	0.74	2.76	1.28	?	Mathieson and Wadsley (1950)
Sitapar, India	5.35	0.90	3.48	1.28	?	Fleischer (1964)
Golconda, Nevada	3.42	0.53	4.16	0.94	Stratified	Kerr (1940)
Boulbab. Morocco	3.03	1.25	none	0.95	Hypogene	Bouladon and Jouravsky (1955)
West Australia	4.4	0.38	0.08	0.79	?	Faulring, Swicker, and Forgeng (1960)
Eisenach, Germany	4.80	—	1.92	0.93	Supergene	Wimmenauer (1955)
Sandur, India	0.09	0.07	0.91	0.08	Supergene	Naganna (1964)

[a] Incomplete analysis, recalculated after deducting braunite.

Other semiquantitative spectrographic analyses of cryptomelane in Table 4 include both hypogene and supergene deposits.

OTHER DEPOSITS

In recent years, beds of manganese oxides have been explored in the Virgin Springs Valley, northern Humboldt County (H. K. Stager, written communication, 1959). Within a section of sedimentary rocks about 50 feet thick that is a part of a much thicker section composed of volcanic ash, silt, sand, and diatomite, there are 17 distinct beds of manganese oxides whose total thickness is 8 feet. According to K. E. Lohman, of the U.S. Geological Survey, the age of the diatoms is late middle Miocene. The principal manganese mineral is cryptomelane, and the semiquanti-

TABLE 4. SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSES OF CRYPTOMELANE[a]

Locality	K	Na	Ba	Mode of origin
Arizona, Apache mine	7.	0.7	1.5	Hypogene
Arizona, Oregon-Prompter mine	3.	—	0.0015	Supergene
Nevada, Virgin Spgs Valley	3.	1.5	.3	Bed
Nevada, Wells Cargo mine	7.	0.7	.7	Hypogene
Nevada, Dixon mine	3.	—	.3	Hypogene
New Mexico, Killion mine	3.	—	.3	Hypogene
New Mexico, Rheinhart mine	7.	—	1.5	Hypogene
Utah, Wild Cat mine	7.	0.3	1.5	Supergene

[a] Chris Heropoulos, analyst.

tative spectrographic analysis of Table 4 indicates about 3 percent potassium.

MODE OF ORIGIN

Only in one other district known to the writers—Mellila, Morocco (Bauchau and Pouit, 1966)—is there as good evidence of a genetic relation of a vein of manganese oxide and a bed of manganese oxide as in the Alcerreca area. In the latter area, a vein and a bed lie in close proximity and the elements in the oxide indicate a genetic relation. There is widespread belief that the silica in some beds of diatoms and radiolaria is derived from volcanic sources. It is thus concluded that at Alcerreca the manganese oxide that forms the bed and the manganese oxide in the nearby vein were both derived from waters of volcanic origin.

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