MANNARDITE [Ba·H$_2$O](Ti$_6$V$_2^{3+}$)O$_{16}$, A NEW MINERAL SPECIES, AND NEW DATA ON REDLEDGEITE

J. DOUGLAS SCOTT AND GILES R. PEATFIELD*

Kidd Creek Mines Limited, P.O. Box 175, Commerce Court West, Toronto, Ontario M5L 1E7

ABSTRACT

Mannardite, a complex oxide of the cryptomelane group, is a new mineral species that occurs as millimetre-sized euhedral black crystals in quartz–carbonate veins on the Rough Claims, near Sifton Pass, northern British Columbia. It is associated with barytocalcite, norsethite and sulvanite. Mannardite has the ideal formula [Ba·H$_2$O] (Ti$_6$V$_2^{3+}$)O$_{16}$. It is opaque in reflected light and pale reddish brown in color, with distinct bireflectance in shades of light to dark brown and strong anisotropism from light pinkish-grey to dark brownish-grey. The cell is tetragonal $I4_1/a$, with edges a 14.356(4), c 5.911(3) Å, $Z = 4$, $D_x = 4.28$, $D_{obs} = 4.12$ g/cm^3. The strongest five lines in the X-ray powder pattern [d in Å(I)(hkl)] are: 3.201(100)(420), 1.586(80)(732), 2.473(70)(312), 1.887(70)(352), 2.224(50)(332).

Redledgeite, isostructural with mannardite, has been determined from holotype crystals to have the ideal formula [Ba·H$_2$O] (Ti$_6$Cr$_2^{3+}$)O$_{16}$. Its cell edges are a 14.320(2), c 5.893(1) Å. X-ray powder patterns of the two species are readily distinguishable on the basis of the line 7.10(20)(200); it is present in redledgeite but absent in mannardite.

Keywords: mannardite, new mineral species, cryptomelane (hollandite) group, new data on redledgeite, water content, British Columbia.

SOMMAIRE

La mannardite, oxyde complexe du groupe de la cryptomelane, nouvelle espèce minérale, se trouve dans des filons de quartz et carbonates, dans les Rough Claims, situés près du col du Sifton, en Colombie-Britannique septentrionale. Elle se présente en cristaux noirs, idiomorphes, dont la taille se mesure en millimètres. Elle est accompagnée de barytocalcite, norsethite et sulvanite. De formule idéale [Ba·H$_2$O](Ti$_6$V$_2^{3+}$)O$_{16}$, opaque en lumière réfléchie et d'un pâle brun rougeâtre, elle possède une biréflectance distincte, de brun clair à brun foncé, et une forte anisotropie, d'un clair gris rosâtre à un sombre gris brunâtre. La maille est tétragonale, de dimensions a 14.356(4), c 5.911(3) Å, $Z = 4$, $D_x = 4.28$, $D_{obs} = 4.12$. Le groupe spatial est $I4_1/a$. Les cinq raies les plus intenses sur le cliché de poudre sont [d en Å(I)(hkl)]: 3.201(100)(420), 1.586(80)(732), 2.473(70)(312), 1.887(70)(352), 2.224(50)(332).

La redledgéite, isotype de la mannardite, analysée sur cristaux holotypes, donne la formule [Ba·H$_2$O]

(Ti$_6$Cr$_2^{3+}$)O$_{16}$ et la maille d'arêtes a 14.320(2), c 5.893(1) Å. Les clichés de poudre, en diffraction X, permettent d'identifier les deux espèces: la raie 7.10(20)(200) de la redledgéite est absente dans la mannardite.

(Traduit par la Rédaction)

Mots-clés: mannardite, nouvelle espèce minérale, groupe de la cryptomelane (hollandite), redledgéite (nouvelles données), contenu d'eau, Colombie-Britannique.

INTRODUCTION

During a routine visit to a lead–zinc prospect in northern British Columbia, one of us (GRP) collected a suite of unusual black crystals in late-stage quartz–carbonate veins. Preliminary X-ray-diffraction examination of the crystals suggested that the material represents a new species, related to redledgeite or priderite. Subsequent study has verified the initial suggestion; however, it has been necessary to determine the crystal structure of the new mineral (Szymański 1986) and to thoroughly re-examine holotype crystals of redledgeite before a final resolution was possible. The name *mannardite* honors the late Dr. George William Mannard (1932–1982), president of Kidd Creek Mines Ltd. It commemorates his long-standing interest in unusual minerals and in the mineral deposits of northern British Columbia; it is particularly appropriate in that Dr. Mannard was himself present at the time of the initial collection of the crystals in 1978 and recognized them as being of an unusual nature. Mannardite is a complex oxide of the cryptomelane group; in Ferraiolo's (1982) classification it would be 7.5.5.1, with redledgeite (as herein described) being 7.5.5.2.

The mineral and the name have been approved by the Commission on New Minerals and Mineral Names of the I.M.A. (mineral 83–13, May 1983). Cotype specimens are preserved in the National Mineral Collection (Geological Survey of Canada) as GSC64197, at the Royal Ontario Museum as M40292 and M40293, and at the British Museum (Natural History) as BM1983,68 and BM1983,69. All metatypes and topotypes available for exchange, amounting to some 100 specimens, have been donated to the National Mineral Collection for distribution at the discretion of the curator.

*Present address: MineQuest Exploration Associates Limited, 311 Water Street, Vancouver, British Columbia V6B 1B8.
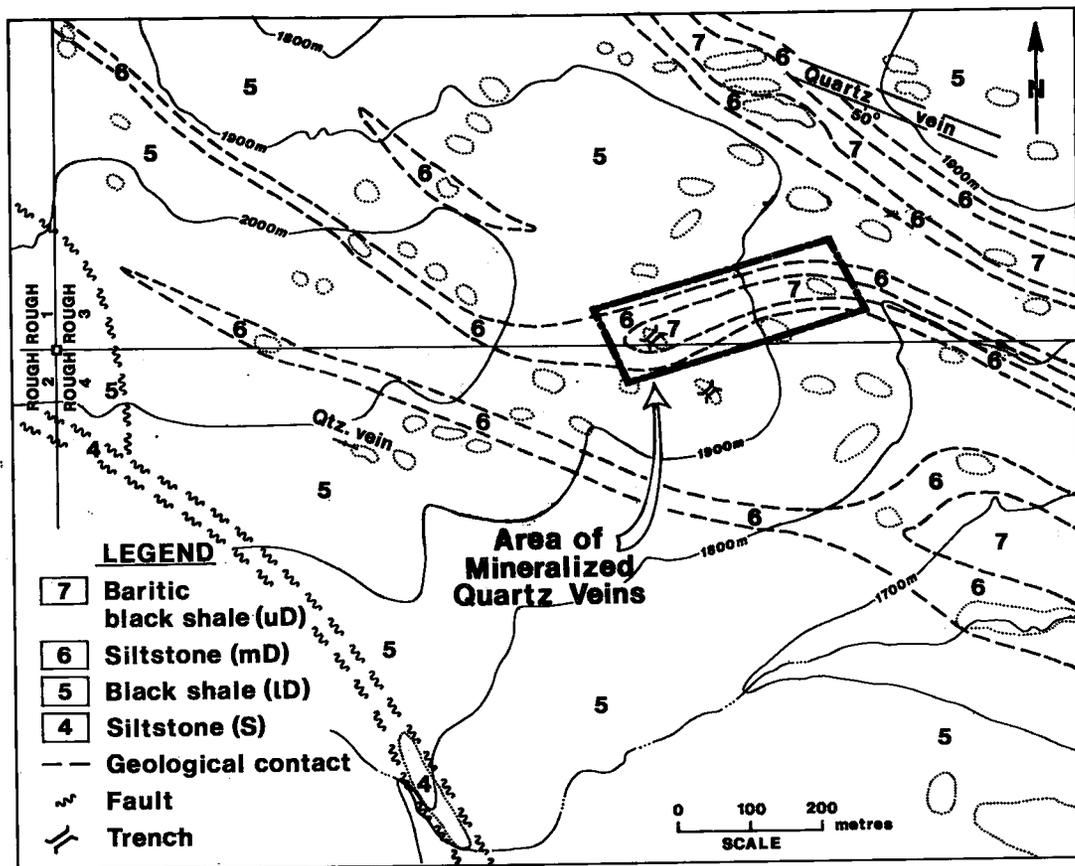
FIG. 1. Map showing the location on the Rough Claims.

OCCURRENCE AND ASSOCIATIONS

Mannardite occurs in narrow quartz–carbonate veins that cut a Devonian shale and siltstone sequence on the Rough Claims (Fig. 1) between the Kechika and Gataga Rivers, north of Sifton Pass, northern British Columbia (126°10′W, 58°16′N, NTS 94L/8E). More specifically, the occurrence is close to the headwaters of Through Creek, near the boundary between the Rough 3 and 4 mineral claims (Boronowski 1982). This property hosts zinc and lead showings in lower Paleozoic strata, and is partly underlain by lithologies favorable as hosts for mineralization of the so-called sedimentary exhalative (sedex) massive pyritic zinc–lead–silver type (Carne & Cathro 1982). In this region, such mineralization occurs in the barite-rich Gunsteel "Formation" near the base of the Middle Devonian – Lower Mississippian Earn or "Black Clastics" Group (MacIntyre 1982, 1983). The most notable sedex deposits in the region are the Driftpile Pass and Cirque deposits,

respectively, some 25 and 100 kilometres to the southeast.

Limited areas on the Rough Claims are underlain by small-fold remnants of Gunsteel strata, with local occurrences of nodular and thin-bedded barite, such as MacIntyre (1983, p. 152) believes "may be the distal equivalents of the massive pyrite and bedded barite deposits." The veins containing mannardite are apparently nearly vertical, cut the Gunsteel and immediately underlying strata, and appear to post-date the folding of the sedimentary strata. No information is available regarding their absolute age.

Three distinct types of mannardite-bearing vein material have been collected to date. Type-A material, which contains the largest crystals of mannardite, is unweathered, massive to somewhat vuggy, milky vein-quartz in which cavities have been completely infilled with crystalline patches up to 1 cm in diameter of cream-colored barytocalcite $CaBa(CO_3)_2$ and elongate flattened crystals of greenish grey norsethite $MgBa(CO_3)_2$. The car-

Barytocalcite		Norsethite		Sulvanite	
BaO	51.4%	BaO	53.3%	Cu	51.6%
CaO	17.9	CaO	1.0	V	14.3
MgO	0.2	MgO	14.3	S	34.2
		MnO	0.8		100.1

12 spot analyses per grain, 20 kV, 10 second counts, standards:
G.S.C. dolomite (CaKα, MgKα), synthetic BaSO₄(BaLα), G.S.C.
rhodochrosite (MnKα), G.S.C. chalcopyrite (SKα), synthetic
V₂O₅(VKα) and synthetic CuFeS224(CuKα).

bonates are essentially stoichiometric (Table 1) and postdate the mannardite. A generation of small euhedral clear crystals of quartz lines the vugs, and mannardite, as euhedral terminated crystals, is found growing within and upon these. Introduction of the carbonates was coincident with a period of fracturing of the quartz vein-material. This fracturing broke or detached many of the free-grown mannardite crystals; therefore, occasional small crystals (<1 mm) of mannardite doubly terminated on {001} are found, apparently free-floating, in the barytocalcite crystals. All mannardite crystals are deeply striated parallel to their elongation and display a prominent {100} cleavage. The larger crystals are flattened parallel to *a*, somewhat bent or twisted parallel to *c*, and have abundant thin quartz-healed fractures normal to [001]; fan-like aggregates of these mannardite crystals attain a maximum size of 3 × 15 mm, though most are less than 5 mm long (Fig. 2).

Type-B material is the weathered equivalent of type A, in which almost all the barytocalcite has been altered to form pockets of very fine-grained powdery white barite. Norsethite is very rare, and the quartz also contains a few crystals of sulvanite Cu_3VS_4 as bronzy black, tarnished cubes to 5 mm in size. In type-B material, the mannardite usually forms radial clumps of terminated crystals in the quartz; the largest crystal observed is 0.5 × 1 × 5 mm, but most crystals are about 0.2 × 0.2 × 1 mm. In general, mannardite appears to be contemporaneous with the sulvanite but earlier than the carbonates and most of the quartz. Type-C material consists of late-stage fracture fillings of columnar quartz centrally cross-cutting type-B veins. Mannardite occurs as elongate needles along the columnar quartz grain-boundaries and is particularly plentiful as small isolated crystals at and near the edges of the veins. There has been minor infilling of tubular voids between the quartz columns with barytocalcite; no other species were observed.

PHYSICAL AND OPTICAL PROPERTIES

Mannardite occurs as shiny jet-black elongate prismatic crystals, with an uneven to subconchoidal fracture and an adamantine lustre; it bears a close macroscopic resemblance to rutile. The crystals are deeply striated parallel to their elongation and display a prominent {100} cleavage. They are usually bounded by {110} prisms and are terminated by {001}; {100} is rare. The streak is white; however, depending on the pressure used and the direction in which the streak is taken, it may appear greyish as
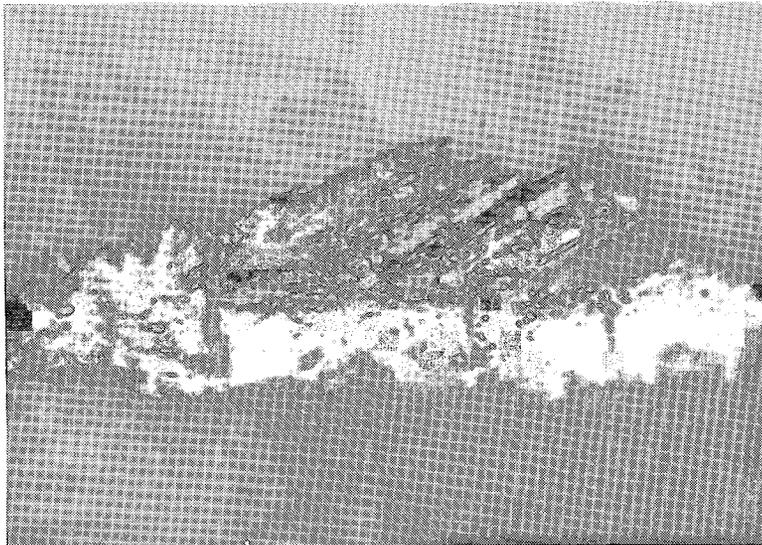
FIG. 2. Fan-like aggregate (not twinned) of two generations of mannardite crystals in quartz. The group is 5 mm long and shows numerous cross-cutting quartz veinlets.

a result of the presence of a host of tiny black nee-
dles. The Mohs hardness is approximately 7;
attempts to determine the Vickers microindentation
hardness, using a Durimet tester, were completely
unsuccessful. The mineral, because of its structure
and brittleness, shattered under the pressure of the
diamond tip even when the minimum load of 10
grams was used. The resulting impressions were
extremely small and so fractured as to be unmeas-
urable. The density, measured by Berman balance
on a very small (1.65 mg) crystal, is 4.12 g/cm³; the
calculated density (for $BaH_2OTi_6V_2O_{16}$) is 4.28
g/cm³.

In reflected light, mannardite is opaque, and even
at very thin edges no internal reflections are
observed. It is pale reddish brown with distinct
bireflectance in shades of light to dark brown, and
strong anisotropism from light pinkish grey (R_o) to
dark brownish grey (R_e). In general, mannardite is
very similar in optical properties to ilmenite. Quan-
titative reflectance measurements were made by A.J.
Criddle of the British Museum (Natural History) at
intervals of 10 nm from 400–700 nm using the equip-
ment and procedures described in Criddle *et al.*
(1984). A SiC standard, Zeiss no. 472, was used for

all measurements. Three crystals, all polished
approximately parallel to prism sections, were meas-
ured. With the exception of some small differences
in R and ^{im}R in the range 400–440 nm (where reflec-
tance data are least reliable because of the optical
train's poor transmission of light), the two groups
of three curves for the two vibration directions are
nearly identical (Fig.3). It was thus impossible to
decide which group corresponds to R_o and which to
R_e', so one crystal was extracted, reoriented and
remeasured as a basal section. R_o and $^{im}R_o$ for this
section are shown as thickened solid lines in Figure
3. The similarity of the R_e' curves for the prism sec-
tions suggests that, by accident, the true R_e was
measured. However, since the orientation of the
prisms was not determined beforehand, the values
are listed as R_e' in Table 2.

Color values for the COM recommended
illuminants A and C (Table 2) are in agreement with
the observed bireflectance–reflectance pleochroism.
The dominant wavelengths for illuminant A for R_o
are blue; however, the excitation purities are very low
(<1%), indicating the proximity to the illuminant
point, and therefore R_o is seen as grey. R_e' appears
light brown by comparison since both excitation
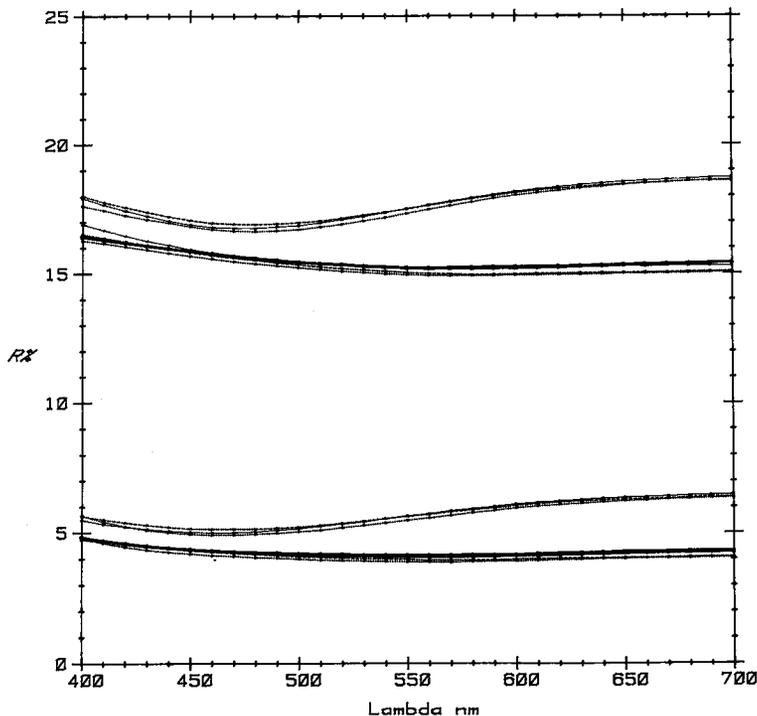
FIG. 3. R and ^{im}R spectra for mannardite. The R spectra are the upper two sets of
curves, R_e' (top) and R_o (bottom). $^{im}R_e'$ and $^{im}R_o$ (lower set) are for three prism
sections and one basal section (thickened solid line).

TABLE 2.   REFLECTANCE DATA FOR MANNARDITE

	AIR							OIL						
	(Basal)	(Prism)						(Basal)	(Prism)					
		1		2		3			1		2		3	
λnm	R_o	R_o	R_e'	R_o'	R_e'	R_o'	R_e'	R_o	R_o	R_e'	R_o	R_e'	R_o	R_e'
400	16.4	16.5	18.0	16.3	17.6	16.9	17.9	4.8	4.75	5.65	4.8	5.7	4.8	5.5
10	16.3	16.4	17.8	16.7	17.5	16.7	17.7	4.7	4.65	5.5	4.6	5.4	4.7	5.3
20	16.2	16.3	17.6	16.05	17.3	16.5	17.45	4.6	4.55	5.4	4.5	5.25	4.6	5.2
30	16.1	16.1	17.4	15.9	17.1	16.3	17.2	4.5	4.5	5.3	4.35	5.1	4.5	5.15
40	16.0	16.0	17.2	15.8	17.0	16.1	17.05	4.4	4.4	5.2	4.3	5.0	4.4	5.1
450	15.9	15.85	17.1	15.7	16.8	15.9	16.9	4.4	4.3	5.2	4.2	5.0	4.4	5.0
60	15.8	15.7	17.0	15.6	16.7	15.8	16.8	4.3	4.3	5.2	4.1	4.9	4.3	5.0
70	15.7	15.6	16.9	15.5	16.7	15.7	16.8	4.3	4.2	5.2	4.1	4.9	4.25	5.0
80	15.6	15.5	16.9	15.4	16.6	15.6	16.8	4.25	4.1	5.0	4.1	5.0	4.2	5.05
90	15.5	15.4	16.95	15.3	16.7	15.55	16.8	4.2	4.1	5.2	4.0	5.0	4.2	5.1
500	15.45	15.4	17.0	15.2	16.7	15.5	16.9	4.2	4.1	5.2	4.0	5.05	4.15	5.2
10	15.4	15.3	17.1	15.2	16.8	15.3	17.0	4.2	4.1	5.3	4.0	5.1	4.1	5.3
20	15.4	15.2	17.2	15.1	16.9	15.3	17.1	4.2	4.05	5.4	3.95	5.2	4.1	5.35
30	15.3	15.2	17.3	15.05	17.05	15.2	17.2	4.15	4.0	5.5	3.9	5.3	4.1	5.4
40	15.3	15.1	17.4	15.0	17.2	15.2	17.4	4.15	4.0	5.6	3.9	5.4	4.1	5.6
550	15.2	15.1	17.5	15.0	17.3	15.2	17.5	4.15	4.0	5.7	3.9	5.5	4.1	5.7
60	15.2	15.0	17.7	14.9	17.5	15.2	17.7	4.15	4.0	5.7	3.9	5.6	4.1	5.75
70	15.2	15.0	17.8	14.9	17.6	15.2	17.8	4.15	4.0	5.8	3.9	5.7	4.1	5.9
80	15.2	15.0	17.9	14.9	17.8	15.2	17.9	4.15	4.0	5.9	3.9	5.8	4.1	5.9
90	15.25	15.0	18.0	14.9	17.9	15.2	18.05	4.2	4.0	6.0	3.9	5.9	4.1	6.0
600	15.25	15.0	18.1	14.9	18.0	15.2	18.2	4.15	4.0	6.1	3.9	6.0	4.1	6.1
10	15.25	15.0	18.2	14.9	18.1	15.2	18.25	4.15	4.0	6.1	3.9	6.0	4.1	6.2
20	15.3	15.0	18.3	14.95	18.2	15.2	18.3	4.2	4.0	6.2	4.0	6.1	4.1	6.2
30	15.3	15.0	18.4	14.95	18.3	15.2	18.4	4.2	4.0	6.2	4.0	6.1	4.1	6.3
40	15.3	15.0	18.4	15.0	18.4	15.25	18.5	4.3	4.0	6.3	4.0	6.2	4.15	6.3
650	15.3	15.0	18.5	15.0	18.4	15.3	18.55	4.3	4.0	6.3	4.0	6.2	4.2	6.35
60	15.35	15.05	18.5	15.0	18.5	15.3	18.6	4.3	4.0	6.3	4.0	6.25	4.2	6.4
70	15.4	15.1	18.55	15.0	18.5	15.3	18.6	4.3	4.1	6.3	4.0	6.3	4.2	6.4
80	15.4	15.1	18.6	15.0	18.6	15.3	18.65	4.3	4.1	6.4	4.0	6.3	4.2	6.4
90	15.4	15.1	18.6	15.0	18.6	15.3	18.7	4.3	4.1	6.4	4.1	6.35	4.2	6.5
700	15.4	15.1	18.6	15.1	18.6	15.3	18.7	4.3	4.1	6.4	4.1	6.4	4.2	6.5

COLOUR VALUES

Illuminant A

x	0.445	0.444	0.453	0.445	0.454	0.445	0.454	0.446	0.443	0.462	0.445	0.464	0.445	0.464
y	0.406	0.405	0.407	0.406	0.407	0.405	0.408	0.405	0.403	0.408	0.403	0.408	0.404	0.409
$Y\%$	15.3	15.1	17.8	15.0	17.6	15.2	17.8	4.2	4.0	5.8	3.9	5.7	4.1	5.8
λ_d	480	484	594	483	594	480	592	c579	475	592	440	592	c579	591
$P_e\%$	0.7	1.0	3.9	0.8	4.6	0.8	4.8	0.7	1.3	10.1	1.0	11.7	1.0	12.5

Illuminant C

x	0.307	0.306	0.316	0.306	0.317	0.307	0.317	0.307	0.304	0.325	0.306	0.327	0.306	0.328
y	0.312	0.310	0.319	0.311	0.319	0.311	0.320	0.310	0.307	0.325	0.307	0.326	0.308	0.328
$Y\%$	15.3	15.1	17.6	15.0	17.45	15.3	17.6	4.2	4.0	5.7	3.9	5.6	4.1	5.7
λ_d	464	470	591	469	590	466	588	440	464	586	451	586	443	584
$P_e\%$	1.6	2.3	2.2	2.0	2.6	2.1	2.8	2.1	3.5	6.2	3.0	7.2	2.7	7.9

c = the complementary wavelength λ_c

purity and luminance are higher and the dominant wavelength is shifted into the yellow-orange.

Indices of refraction and absorption coefficients (Fig. 4) were computed using the Koenigsberger equations as described by Embrey & Criddle (1978). Mannardite is uniaxial positive with very little dispersion of the birefringence or biabsorption. It will be noted that n_o, measured on four sections, and n_e', on three, are remarkably consistent and constant. The k_e' values are, however, more regular than the k_o values, and the biabsorption changes sign below 450 nm. The angles of intersection of the R and ^{im}R curves are, with the exception of one set, all above 5°. This set, where the angles fall as low as 3°, produces jagged absorption curves for k_o and an imaginary value at 400 nm. The constancy of n_e'

and k_e' reinforces the belief that, by accident, the true extraordinary vibration direction was measured. The mean calculated indices of refraction are therefore ω 2.26(1) and ϵ 2.42(1).

MINERAL CHEMISTRY

Three crystals of mannardite in polished section were analyzed using an ARL microprobe (D.R. Owens, analyst) under the following conditions of analysis: accelerating voltage 20 kV, specimen current 0.030 μA, and counting periods of 10 seconds duration for a minimum of 10 counts from both standards and specimen. The following standards and X-ray-emission lines were used: synthetic
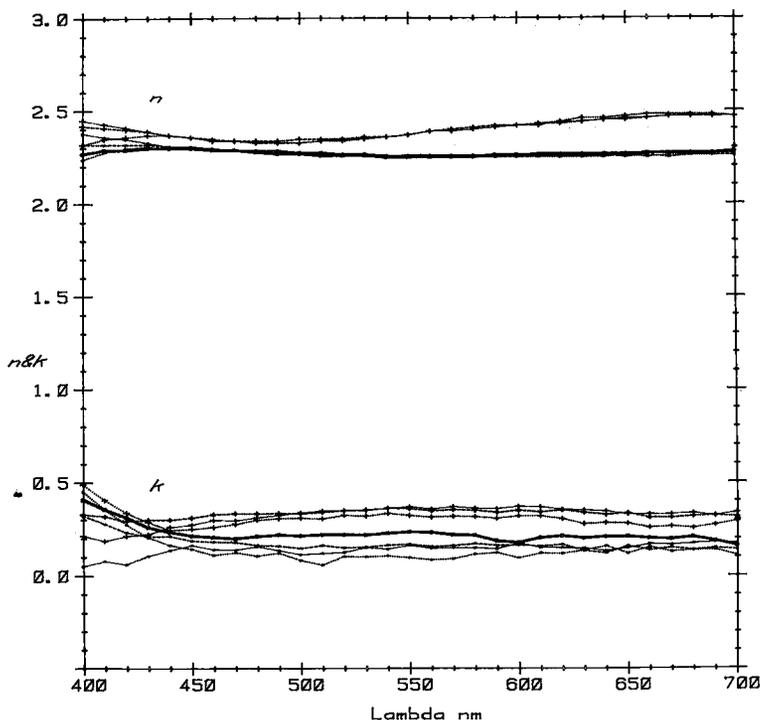
FIG. 4. Indices of refraction (upper set of curves) and absorption coefficients (lower set) for mannardite. In both sets, the lower group corresponds to the ordinary vibration-direction.

$BaSO_4$ ($BaL\alpha$), synthetic V_2O_5 ($VK\alpha$), synthetic TiO_2 ($TiK\alpha$) and natural chromite (standard GS3, G.S.C. analyzed) ($CrK\alpha$).

All four elements were determined using wavelength-dispersion spectrometers equipped with sealed proportional counters and LiF analyzing crystals. Ti was analyzed simultaneously with Ba, and Cr with V. Because of the problems with peak overlap between $TiK\alpha_1$ and $BaL\alpha_1$, the two spectrometers were equipped with aligned 0.03-mm slits; this reduced the overlap to an almost negligible amount. These slits also limited the direct enhancement of $VK\alpha_1$ by both $TiK\beta_1$ and $BaL\beta_3$, and of $CrK\alpha_1$ by $VK\beta_1$. The crystals were also analyzed to determine if trace amounts of Na, Mg, K, Al, Si, Fe or Ni were present; none of these was detected. The limits of detection for the above elements was calculated to be approximately 400, 350, 300, 350, 350, 300 and 300 ppm, respectively. The data resulting from these analyses (Table 3) were refined at CANMET, using a locally modified version (ERPMAG) of the EMPADR VII computer program of Rucklidge & Gasparrini (1969).

Examination of simultaneous counts in the individual spot-analyses showed that V is highly correlated with Cr (–0.93), and all of the compositions cluster about the tie line $BaTi_6V_2O_{16}$–$BaTi_6Cr_2O_{16}$ (Fig. 5). In order to determine if there is any systematic variation away from this line within a single grain, a 1-mm crystal was analyzed at 10 random points with a four-spectrometer Cameca microprobe. The average of these compositions (Table 3, grain 4) falls close to the tie line, and all points are within the previously defined cluster. Mannardite crystals are thus inhomogeneous on a "micro" scale. Local variations in the extent of trivalent substitution in the titanium site are balanced by simultaneous changes in the barium occupancy, such that within any unit cell of formula $[Ba_x(H_2O)_{2-x}]Ti_yM_zO_{16}$, where M is trivalent V, Cr or Fe, the equations $2x + 4y + 3z = 32$, $y + z = 8$ and $z = 2x$ are satisfied. The formula for type mannardite as determined by the crystal-structure analysis (Szymański 1986) is $[Ba_{1.03}(H_2O)_{0.97}](Ti_{5.97}V_{1.76}Cr_{0.27})O_{16}$, which fits this model exactly.

Lithium, detected by emission spectrography, was determined in three crystals by Secondary Ion Mass Spectrometry (SIMS) through the courtesy of Dr. N.S. McIntyre of the University of Western Ontario. The lithium content of mannardite appears to vary erratically between 0.02 and 0.06 wt.%. It is not an essential component of the mineral.

TABLE 3. MICROPROBE DATA ON MANNARDITE

Grain 1*				Atoms (O=16)		Element Range
Ba	18.0	BaO	20.1	Ba	1.07	17.5 to 18.7%
Ti	34.5	TiO_2	57.5	Ti	5.88	33.6 to 35.5
V	11.0	V_2O_3	16.2	V	1.77	10.4 to 11.6
Cr	2.2	Cr_2O_3	3.2	Cr	0.34	2.1 to 2.6
			97.0			

Grain 2*						
Ba	17.8%	BaO	19.9%	Ba	1.06	17.0 to 18.6%
Ti	34.3	TiO_2	57.2	Ti	5.87	33.5 to 35.8
V	11.3	V_2O_3	16.6	V	1.82	10.7 to 11.8
Cr	2.0	Cr_2O_3	2.9	Cr	0.31	1.5 to 2.4
			96.6			

Grain 3**						
Ba	17.4%	BaO	19.4%	Ba	1.02	
Ti	36.0	TiO_2	60.1	Ti	6.03	
V	11.1	V_2O_3	16.3	V	1.75	
Cr	1.3	Cr_2O_3	1.9	Cr	0.20	
			97.7			

Grain 4 (Cameca analysis)						
Ba	16.5%	BaO	18.4%	Ba	0.96	16.2 to 17.1%
Ti	35.9	TiO_2	59.9	Ti	6.00	34.9 to 36.5
V	10.7	V_2O_3	15.8	V	1.68	10.0 to 11.2
Cr	2.1	Cr_2O_3	2.9	Cr	0.32	1.6 to 2.7
			97.2			

Brunswick No. 12 (GSC 14973)						
Ba	17.7%	BaO	19.8%	Ba	1.04	
Ti	36.1	TiO_2	60.2	Ti	6.07	
V	8.3	V_2O_3	12.2	V	1.32	
Cr	1.3	Cr_2O_3	1.9	Cr	0.20	
Fe	2.6	Fe_2O_3	3.7	Fe	0.38	
			97.8			

* 15 spot analyses per grain
** grain from which the crystal structure was determined

Analytical sums including the channel water molecules, calculated on the basis of 2 minus Ba, are: 99.1, 98.7, 99.9, 99.6 and 100.0, respectively.

The role of water in mannardite was only clarified after the crystal structure was refined to a residual R of 0.029 (Szymański 1986). The mineral shows no signs of the typical deterioration under the electron beam that is observed with either hydrous species or those that contain zeolitic water in open channels. The low analytical totals (Table 3) were therefore a considerable source of concern in the early stages of this work. Re-examination of the SIMS data, which had been taken on polished sections of mannardite crystals, showed strong peaks for atomic weights of 1(H) and 17(OH). The hydrogen peak was used to calculate the water content of mannardite, based on the lepidolite standard used in the lithium analyses; this value is 2.1 ± 0.2%, or almost exactly one H_2O molecule per formula unit. The channel-site barium atoms form a one-dimensional grid, trapping between them water molecules that are only hydrogen-bonded to the oxygen atoms of the channel wall. The two-fold barium site is thus actually occupied by $[Ba_x(H_2O)_{2-x}]$, where x is approximately 1, rather than by a barium atom and a vacant position as was initially supposed. This water cannot be driven off below the temperature at which the crystal structure is destroyed.

X-RAY CRYSTALLOGRAPHY

A single-crystal X-ray-diffraction study of a
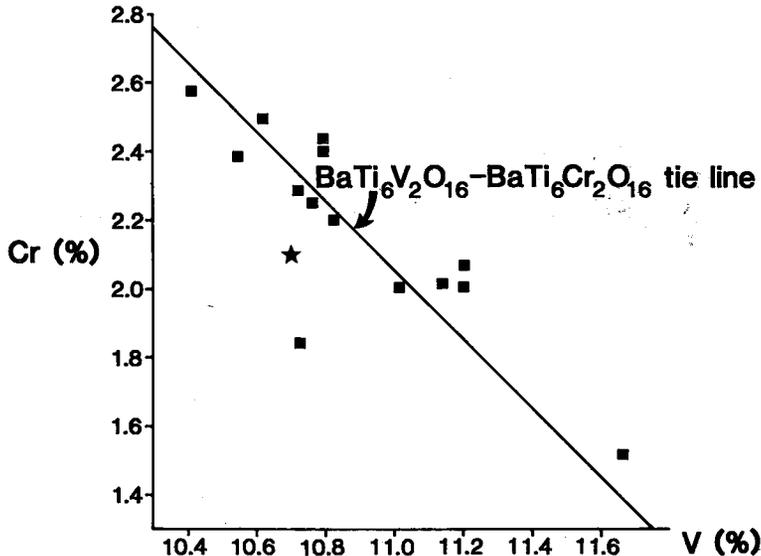
FIG. 5. Results of simultaneous microprobe spot-analyses for V and Cr on one mannardite crystal. The star indicates both a point in the set and the average value from 10 four-element Cameca analyses.

TABLE 4. X-RAY POWDER DATA FOR MANNARDITE AND REDLEDGEITE

	Mannardite				Redledgeite	
Iobs	Icalc	dÅ obs	dÅ calc	hkl	I	dÅ obs
–	2	–	7.18	200	20	7.10
–	9	–	5.076	220	5	5.05
20	23	3.587	3.582	400	50	3.570
100	100	3.201	3.204	420	100	3.195
10	11	2.836	2.833	112	30	2.831
–	4	–	2.538	440	10	2.536
70	50	2.473	2.472	312	60	2.470
30	20	2.264	2.266	620	30	2.257
50	43	2.224	2.222	332	40	2.217
10	10	2.031	2.035	152	30	2.033
20	7	1.985	1.987	460	30	1.985
70	30	1.887	1.888	352	50	1.885
5	4	1.792	1.791	800	20	1.788
5	4	1.737	1.738	820	20	1.735
50	20	1.690	1.689	660	40	1.685
80	32	1.586	1.586	732	60	1.583
20	8	1.475	1.475	004	30	1.474
5	6	1.452	1.451	572	20	1.448
40	23	1.394	1.394	192	50	1.393
20b	15	1.341	1.340	424,392	20	1.339
20b	9	1.332	1.330	10.4.0,772	20	1.325
–	4	–	1.238	624	10	1.234
10	4	1.192	1.194	12.0.0	10	1.193
10	3	1.156	1.156	11.3.2,972	10	1.154
10	1	1.139	1.139	804	–	–
10	4	1.119	1.119	10.8.0	20	1.117
20	8	1.111	1.111	664	20	1.109
10b	1	1.070	1.068	12.6.0	–	–
10	6	1.030	1.030	13.1.2,7.11.2	20	1.027
10	4	1.010	1.009	3.13.2	10	1.007

Note: Visually estimated intensities from 114.6-mm camera, with Co radiation, calculated intensities from the refined crystal-structure parameters; since I(hkℓ)≠I(khℓ), the strongest line of the superimposed doublet is given.

cleavage fragment of mannardite, initially mounted with c as the dial axis on the precession camera, showed the mineral to be tetragonal, and uniquely determined the space group as $I4_1/a$ (number 88). Odd levels in c are weak but display sharp Bragg reflections, superimposed on a continuous sheet of diffuse scattering. There is no vestige of incommensurate superlattice-ordering. The unit-cell parameters, refined on the basis of 15 uniquely indexed powder-diffraction lines, are a 14.356(4), c 5.911(3) Å, V 1218.23 Å^3, $Z = 4$.

The powder pattern (Table 4) was obtained on a 114.6-mm Debye–Scherrer camera with iron-filtered Co$K\alpha$ radiation. The calculated intensities were derived by the POWGEN program of the XRAY-76 system (Stewart et $al.$ 1976) on the basis of the crystal structure refined to an R of 3.6%. All strong lines ($I > 5$ on a scale of 100) of the calculated pattern were observed, with the exception of three at low angles [d in Å(I)(hkl)]: 5.463(9)(101), 5.076(9)(220) (a line present in the priderite and redledgeite patterns), and 4.347(11)(211). The (200) line at d 7.178 Å, which is clearly observed on the priderite and redledgeite patterns, has a calculated intensity of 2 for mannardite.

FIG. 6. Redledgeite (USNM 95846) with intergrown chromian clinochlore; backscattered-electron image shows the compositional homogeneity of both species.

TABLE 5. MICROPROBE DATA ON CHROMIAN CLINOCHLORE

	USNM 95846	GSC 17105
MgO	33.2%	32.5%
FeO	0.9	0.5
Cr$_2$O$_3$	9.4	12.0
Al$_2$O$_3$	10.4	9.4
SiO$_2$	31.7	31.2
	85.6	85.6

10 spot analyses per grain, four grains per sample, 20 kV, 10 second counts, standards: synthetic forsterite (Mg$\underline{K}\alpha$, Si$\underline{K}\alpha$), kaersutite (Fe$\underline{K}\alpha$, Al$\underline{K}\alpha$) and chromite (Cr$\underline{K}\alpha$).

A SECOND OCCURRENCE OF MANNARDITE

Mannardite has recently been found (by H.G. Ansell of the Geological Survey of Canada) in material from the Brunswick No. 12 orebody, Bathurst, New Brunswick. It occurs there with crystals of edingtonite (Grice et $al.$ 1984), harmotome, barytocalcite, siderite, sphalerite and quartz on a single specimen (GSC 14973) from the 13/16 N(E) stope on the 2350 level. This area of the east ore-zone was severely sheared and fractured when the footwall metasediments were folded around the hanging-wall iron formation. The late-stage mineral assemblage occurs as euhedral crystals in open fractures. Mannardite, as 1-mm-long euhedral tetragonal rods implanted on quartz crystals, appears to have been the last mineral formed; its composition (Table 3) is iron-rich in comparison with the type material.

Chen et $al.$ (1984) recently described the occurrence of chromium-free mannardite from a silver-rich polymetallic deposit at Kantsi, Sichuan Province, China. The associations reported are very similar to those of the Brunswick No. 12 material, and the physical properties are essentially identical with type mannardite. New data are the microindentation hardness at 609 kg/mm^2 (Mohs 5.5 to 6) and the density at 4.43 g/cm^3. The infrared absorption spectrum (not illustrated) is reported to prove that "the mineral contains no water or hydroxyl."

REDLEDGEITE

The mineral now known as redledgeite was originally proposed, on the basis of a chemical analysis, as the new species "chromrutile" (Gordon & Shannon 1928). Two small crystals from the holotype specimen (USNM 95846) were examined by Strunz (1961, 1963), who obtained a density, unit cell, space group and powder pattern from them; on this basis, he recast the original chemical data and renamed the species *redledgeite*, with a cryptomelane-type cell: $8[(Mg,Ca,OH,H_2O)_{\leqslant 2}(Ti_6Si_{0.5}Cr^{3+}_{1.5})O_{16}]$.

It was obvious from the outset of our work on mannardite that its powder pattern and that of redledgeite are essentially identical in both line spacings and intensities, indicating that the two minerals could be isostructural; however, the formulas were strongly divergent, and either the unit cell or the space group proposed by Strunz did not fit with the mannardite data. We obtained and examined crystal fragments of holotype redledgeite (USNM 95846). It was immediately apparent that the mineral is intimately and finely intergrown with light pink crystals of kammererite (chromian clinochlore) (Fig. 6, Table 5).

This observation threw the results of the original wet-chemical analysis into question. Precession photographs of a "pure" fragment confirmed the space group as $I4_1/a$. A 25-reflection unit-cell refinement on a CAD-4 diffractometer led to the parameters: a 14.320(2), c 5.893(1) Å. The newly defined cell and confirmed space-group allow complete indexing of a powder pattern made from fragments of the same crystal (Table 4). The powder pattern is in excellent agreement with that published for redledgeite by Strunz (1963), but appears somewhat better resolved and shows the (200) line at d 7.10 Å rather than 7.37 Å. Redledgeite is isostructural with mannardite.

There are, however, additional very weak diffuse reflections in the *l*-odd levels of redledgeite (Fig. 7). Precession photographs show these to be close to, but displaced by a *constant* amount "outward" from, Bragg positions that would negate the body centring of the cell (*i.e.*, at positions with $h + k$ odd when *l* is odd). Determination of the precise position of these diffuse reflections is essentially impossible, but it appears that the diffuse central reflection of any "square" of sharp Bragg peaks is displaced from the centroid by the same amount
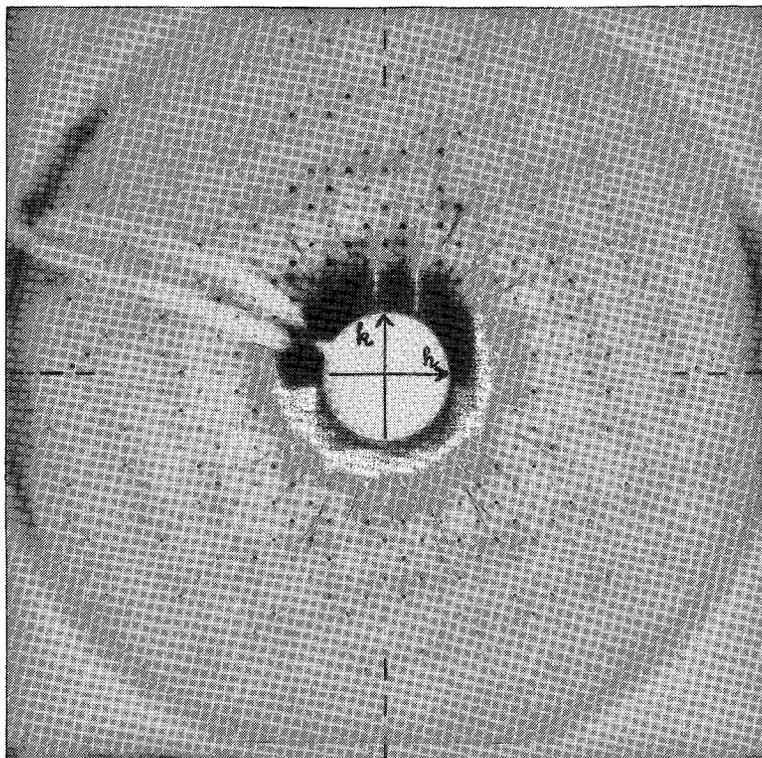
FIG. 7. Precession photograph of the *hk*1 net for redledgeite, taken with filtered MoKα radiation ($\mu = 25°$, 44 kV, 20 mA, 24-day exposure). Between the sharp stronger reflections there are weaker diffuse reflections, close to positions that violate the body-centring condition but slightly displaced away from the origin.

TABLE 6. MICROPROBE DATA ON REDLEDGEITE

Grain 1 (USNM 95846)				Atoms (0=16)		Element Range
Ba	18.1%	BaO	20.2	Ba	1.06	17.5 to 18.5%
Ti	35.8	TiO$_2$	59.7	Ti	6.00	34.2 to 36.9
Cr	11.9	Cr$_2$O$_3$	17.4	Cr	1.84	10.6 to 13.2
V	0.3	V$_2$O$_3$	0.4	V	0.05	0.1 to 0.4
Fe	0.6	Fe$_2$O$_3$	0.9	Fe	0.09	0.3 to 1.1
			98.6			
Grain 2 (USNM 95846)						
Ba	18.4	BaO	20.6	Ba	1.08	18.2 to 18.5
Ti	35.4	TiO$_2$	59.1	Ti	5.98	34.2 to 36.3
Cr	11.7	Cr$_2$O$_3$	17.1	Cr	1.82	9.9 to 12.6
V	0.3	V$_2$O$_3$	0.4	V	0.05	0.2 to 0.4
Fe	0.8	Fe$_2$O$_3$	1.1	Fe	0.12	0.6 to 1.6
			98.3			
Grain 3 (BM 1928, 336)*						
Ba	18.6	BaO	20.8	Ba	1.10	
Ti	35.1	TiO$_2$	58.6	Ti	5.95	
Cr	11.6	Cr$_2$O$_3$	17.0	Cr	1.81	
V	0.5**	V$_2$O$_3$	0.7	V	0.08	
Fe	0.7	Fe$_2$O$_3$	1.0	Fe	0.10	
			98.1			
Grain 4 (GSC 17105)						
Ba	19.1	BaO	21.3	Ba	1.15	
Ti	32.1	TiO$_2$	53.5	Ti	5.53	
Cr	15.9	Cr$_2$O$_3$	23.2	Cr	2.52	
V	0.2	V$_2$O$_3$	0.3	V	0.03	
Fe	<0.03	–		Fe	–	
			98.3			

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* R.F. Symes analysis (average of 20 spot analyses) on a
Cambridge Instruments Microscan 9, at 20 kV, using
barite, synthetic barium fluoride, Cr and Fe metals and
synthetic rutile as standards; ZAF corrected.
** Energy dispersive value (15 kV)
Analytical sums including the channel water molecules,
calculated on the basis of 2 minus Ba, are: 100.7,
100.3, 100.1 and 100.1, respectively

regardless of the absolute value of the indices h and k. A possible explanation of their appearance is that they represent reflections that are incommensurate in c; that is, they lie on a reciprocal plane slightly displaced "below" the primary l-odd levels. Thus their fuzzy appearance and constant displacement are artifacts of the precession method. This would imply both that the barium atoms (and water molecules) in the two tunnel sites of redledgeite are more fully ordered in c than those of mannardite and also that there is some extended relationship between the barium atoms in more than one tunnel, which violates the body-centred condition of the cell. Because of the considerable diffuse scattering in the odd levels of c, no crystal-structure refinement of redledgeite is planned.

Electron-microprobe analyses (Table 6) on two crystal fragments of holotype redledgeite, done under the same operating conditions as for mannardite, show the mineral to be the chromium analog of mannardite and lead to the formula [Ba$_{1.07}$(H$_2$O)$_{0.93}$] (Ti$_6$Cr$_{1.83}^{3+}$V$_{0.05}^{3+}$Fe$_{0.11}^{3+}$)O$_{16}$; an analysis of a third grain from the type locality, by Dr. R.F. Symes at the British Museum (Natural History), gave a very similar result (Table 6). No additional elements were detected in any of the analyses on 100-second counts. Magnesium and silicon in particular are not present in amounts greater than 350 ppm. This proves that

either the original wet-chemical analysis was done on "chromrutile" that included some 17% of accessory kammererite and was also in gross error as to the remaining elements, or both redledgeite and another mineral (chromrutile?) are present on the holotype specimen. It is difficult to believe that an analyst of Shannon's expertise could have missed 20% BaO in a mineral, or have mistaken it for TiO$_2$.

Subtraction of 17% kammererite (Shannon 1921) from the original data results in a formula very close to CrTi$_4$O$_{10}$. Is this perhaps "chromrutile"? There is one further piece of evidence suggesting that redledgeite and "chromrutile" may be two separate species. Shannon (Gordon & Shannon 1928) gave the crystal class of chromrutile as tetragonal bipyramidal (4/m) and the polar ratio p_o as 0.611. Redledgeite is indeed class 4/m, but $p_o(= c)$ is equal to 0.4115 for our material.

A second specimen of redledgeite, recently collected from the type locality (Red Ledge mine, Nevada County, California), was obtained through the courtesy of Forrest Cureton (Cureton Mineral Company). This specimen (now catalogued as GSC 17105) shows small black elongate grains of redledgeite in a groundmass of translucent, light green, extremely fine-grained acicular tetragonal crystals. These minute needles are 0.5 μm thick and cling with great tenacity to the larger crystals of redledgeite. In polished section at high power (oil immersion), the large "black" redledgeite grains are seen to have distinct green internal reflections, which become brighter and more prevalent as the grains thin near their edges. The large grains also appear to grade evenly into the attached translucent-green acicular crystals. A comparison of energy-dispersion spectra obtained from the centre of a redledgeite grain (grain 4, Table 6) and from the largest of the acicular crystals, 2 μm in width, shows these to be of similar composition. Unfortunately, none of the acicular crystals are of sufficient diameter to attempt a quantitative electron-microprobe analysis. X-ray-diffraction patterns obtained from a holotype crystal of redledgeite, from one of the large grains, and from carefully separated pale green needles, are essentially identical, with only minor variations being observed in line intensities; the 7.10-Å line shows up clearly in all three patterns. It is therefore apparent that the pale green acicular crystals are a form of redledgeite. This conclusion was independently reached by Dr. R.F. Symes of the British Museum (Natural History), who examined fibrous green material similar to that of GSC 17105 and concluded that "the BaO content of the fibres is within experimental error of, or slightly higher than (up to 23.6% BaO), the holotype but TiO$_2$ is down and Cr$_2$O$_3$ up in comparison with that analysis" (pers. comm., 1983). On the basis of this observation, a

progressive change in the color of redledgeite from black to green with increasing chromium content is inferred. The data of Table 6 support this: grains 1, 2 and 3 are black with no visible internal reflections and of nearly identical composition; grain 4 on the other hand has vivid green internal reflections, is iron-free and contains less Ti and more Cr than is shown in the first three analyses.

Also found in the groundmass of acicular redledgeite needles were occasional 5-μm brilliant green transparent euhedral trapezohedral crystals. These have the approximate composition: Cr 20%, Mg 15%, Al 4%, Si 18%, Ca and Fe not detected; these data fit well with a near end-member knorringite garnet $Mg_3Cr_2(SiO_4)_3$.

DISCUSSION

Mannardite and redledgeite (as defined above) form the two end-members of an assumed solid-solution series, isostructural at the subcell level, between $(Ba \cdot H_2O)(Ti_6V_2^{3+})O_{16}$ and $(Ba \cdot H_2O)(Ti_6Cr_2^{3+})O_{16}$. Both minerals are of the cryptomelane or nonstoichiometric stuffed type, in which tunnel cations (Ba^{2+}) are present in the structure in amounts that theoretically can vary over a wide range but that appear to be restricted to values of 1 ± 0.1 atoms in the minerals studied. Charge balance within the structure is maintained by the existence of variable proportions of two oxidation states of transition-metal ions within the same octahedrally co-ordinated tunnel-wall (M) sites. In mannardite these are two independent fully occupied general (16-fold) positions randomly filled by ($Ti_{6.05}^{4+}V_{1.75}^{3+}Cr_{0.20}^{3+}$). The mean M–O bond lengths for the two sites are identical [1.971(26), 1.972(27) Å], confirming that the transition-metal substitution is purely statistical. This type of solid solution was first defined by Wadsley (1955), who stated that "a host [in this case TiO_2], crystallizing in the presence of ions incapable of substitution, may form a new phase embodying tubes or tunnels which afford the foreign ions [in this case Ba] a normal environment and will not necessarily require integral numbers in a unit formula." In the present case the assumed solid-solution is not one- but two-dimensional in chemical space. Limited cryptomelane-type variations are possible in the nonstoichiometric $Ba_x:M_8$ ratio as a result of the degree of substitution of trivalent ions in the M site. Also, there appears to be the potential for unlimited Cr^{3+} for V^{3+} or Fe^{3+} substitution within the M site at a semifixed titanium content near 6 atoms, implying a continuous solid-solution series between mannardite, redledgeite and a suspected but as yet undefined Fe-analog (cf. Table 3, Brunswick No. 12 sample).

Data for synthetic barium–titanium–chromium hollandite isomorphs (Cadée & Verschoor 1978; D.J.W. Ijdo, pers. comm. 1983) show that the stability field of the mineral herein referred to as redledgeite does not extend into the dry system. For synthetic compositions with 5.74 Ti atoms, a tetragonal $I4/m$ cell isostructural with priderite is observed. This persists to 5.30 Ti atoms, whereupon a monoclinic $I2/m$ cell isostructural with hollandite is found; note that redledgeite compositions as low as 5.53 Ti atoms (grain 4, Table 6) are observed. The redledgeite cell was not synthesized; however, as one-to-two-week-long high-temperature (1200°C) dry fusions were used, and as redledgeite is a low-temperature (less than 200°C is inferred from Grice et al. 1984) hydrothermal mineral, this is perhaps not too surprising. Nevertheless, it suggests that the content of nonbonded water in these species is actually structurally essential insofar as it acts to stabilize the minerals.

Redledgeite can be distinguished from mannardite by X-ray diffraction on the basis of a clearly defined weak (200) line at d 7.10 Å; no sample of mannardite from either of its two localities shows any trace of this line, even on very long exposures. There are several line-intensity differences between the two powder patterns; these are quite obvious on direct comparison of films. Redledgeite also shows faint (220) and (440) reflections, which are not present on the mannardite films. The possibility of chlorite contamination of the redledgeite pattern can be eliminated by the appearance of the 7.10 Å line for both crystal forms of redledgeite on GSC 17105, a specimen that contains no associated or intergrown chlorite.

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