MANNARDITE \([\text{Ba-H}_2\text{O}](\text{Ti}_6\text{V}^{3+}\text{Cr}^{3+})\text{O}_{16}\), 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 \([\text{Ba-H}_2\text{O}](\text{Ti}_6\text{V}^{3+}\text{Cr}^{3+})\text{O}_{16}\). 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 \(a/l, a = 14.356(4), c = 5.911(3)\ \text{Å}, Z = 4\), \(D_x = 4.28, D_{\text{obs}} = 4.12\ \text{g/cm}^3\). The strongest five lines in the X-ray powder pattern \([d \in \text{Å}(hkl)]\) are: 3.20(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 \([\text{Ba-H}_2\text{O}](\text{Ti}_6\text{Cr}^{3+})\text{O}_{16}\). Its cell edges are \(a = 14.320(2), c = 5.893(1)\ \text{Å}\). X-ray powder patterns of the two species are readily distinguishable on the basis of the line 2.10(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.

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.
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/88). 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 postdate 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(CO₃)₂ and elongate flattened crystals of greenish grey norsethite MgBa(CO₃)₂. The car-
MANNARDITE AND REDLEDGEITE

Norsothil€ Sulvanibe

<table>
<thead>
<tr>
<th></th>
<th>Barytocalcite</th>
<th>Norsethite</th>
<th>Sulvanite</th>
</tr>
</thead>
<tbody>
<tr>
<td>BaO</td>
<td>51.4%</td>
<td>53.3%</td>
<td>51.6%</td>
</tr>
<tr>
<td>CaO</td>
<td>17.9</td>
<td>1.0</td>
<td>14.3</td>
</tr>
<tr>
<td>MgO</td>
<td>0.2</td>
<td>14.3</td>
<td>24.2</td>
</tr>
<tr>
<td>MnO</td>
<td>0.8</td>
<td></td>
<td>100.3</td>
</tr>
</tbody>
</table>

12 spot analyses per grain, 20 kV, 10 second counts, standards: G.S.C. dolomite (CaO, MgO), synthetic BaSO4(BaO), G.S.C. rhodochrosite (MnO), G.S.C. chalcopyrite (CuO), synthetic V2O5 and synthetic CuFeS2(FeO).

Carbonates 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 $3 \times 15$ 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$_3$VS$_4$ 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 $0.5 \times 1 \times 5$ mm, but most crystals are about $0.2 \times 0.2 \times 1$ 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
a result of the presence of a host of tiny black needles. 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 unmeasurable. The density, measured by Berman balance on a very small (1.65 mg) crystal, is 4.12 g/cm³; the calculated density (for BaH₂OTi₆V₂O₁₆) 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 (R₁) to dark brownish grey (R₂). In general, mannardite is very similar in optical properties to ilmenite. Quantitative 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 equipment 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 measured. With the exception of some small differences in R and ²R in the range 400–440 nm (where reflectance 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 R₀ and which to Rₑ', so one crystal was extracted, reoriented and remeasured as a basal section. R₀ and ²R₀ for this section are shown as thickened solid lines in Figure 3. The similarity of the Rₑ' curves for the prism sections suggests that, by accident, the true Rₑ was measured. However, since the orientation of the prisms was not determined beforehand, the values are listed as Rₑ' 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 R₀ are blue; however, the excitation purities are very low (<1%), indicating the proximity to the illuminant point, and therefore R₀ is seen as grey. Rₑ' appears light brown by comparison since both excitation...
MANNARDITE AND REDLEDGEITE

TABLE 2. REFLECTANCE DATA FOR MANNARDITE

<table>
<thead>
<tr>
<th>Air</th>
<th>Gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Basal)</td>
<td>(Prism)</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>λnm</td>
<td>R_p</td>
</tr>
<tr>
<td>400</td>
<td>16.9</td>
</tr>
<tr>
<td>600</td>
<td>15.7</td>
</tr>
<tr>
<td>800</td>
<td>15.5</td>
</tr>
<tr>
<td>1000</td>
<td>15.3</td>
</tr>
<tr>
<td>1200</td>
<td>15.1</td>
</tr>
<tr>
<td>1400</td>
<td>14.9</td>
</tr>
<tr>
<td>1600</td>
<td>14.7</td>
</tr>
<tr>
<td>1800</td>
<td>14.4</td>
</tr>
<tr>
<td>2000</td>
<td>14.2</td>
</tr>
<tr>
<td>2200</td>
<td>14.0</td>
</tr>
<tr>
<td>2400</td>
<td>13.8</td>
</tr>
<tr>
<td>2600</td>
<td>13.6</td>
</tr>
<tr>
<td>2800</td>
<td>13.4</td>
</tr>
</tbody>
</table>

The reflectance data for mannardite and redledgeite are given in Table 2. The data show that the reflectance increases with increasing wavelength, and that the reflectance is highest in the ultraviolet region.

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_p, measured on four sections, and n_e, on three, are remarkably consistent and constant. The k_e values, however, are more regular than the k_p values, and the biabsorption changes sign below 450 nm. The angles of intersection of the R and R_e' 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_p 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 2.261(1) and e 2.421(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...
BaSO₄ (BaLa), synthetic V₂O₅ (VKα), synthetic TiO₂ (TiKα) and natural chromite (standard GS3, G.S.C. analyzed) (CrKα).

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 TiKα and BaLa1, 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 VKβ₁ by both TiKβ₁ and BaLβ₁, and of CrKα₁ by VKβ₁. 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 Ba₅Ti₆V₆O₁₈–Ba₅Ti₆Cr₃O₁₈ (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 [Ba₁₋ₓ(H₂O)ₓ]₂₋ₓ TiₓM₂O₁₆, where M is trivalent V, Cr or Fe, the equations 2x + 4y + 3z = 32, x + z = 8 and z = 2x are satisfied. The formula for type mannardite as determined by the crystal-structure analysis (Szymański 1986) is [Ba₁₋₀₃,H₂O]₀₋₀₉₇(Ti₅₋₀₇,V₁₋₀₇₆,Cr₀₋₀₂₇)O₁₆, 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.
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 $2.1 \pm 0.2$, or almost exactly one H$_2$O 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 $[\text{Ba}_x(\text{H}_2\text{O})_{2-x}]$, 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.](image-url)
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 \(a = 14.356(4), c = 5.911(3) \text{ Å}, V = 1218.23 \text{ Å}^3, Z = 4\).

The powder pattern (Table 4) was obtained on a 114.6-mm Debye–Schererrer camera with iron-filtered CoK\(\alpha\) 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 \([d \approx 14(\AA)(hk\ell)]\): 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.

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 13116 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: $8[(Mg,Ca,OH,H_2O)\_2(Ti_{6}Si_{12}Cr)_{12}O_{36}]$.

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 clinohore) (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 $hk1$ net for redledgeite, taken with filtered MoKα radiation ($\lambda = 25^\circ$, 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.
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 $[\text{Ba}_{1.67}(\text{H}_2\text{O})_7]\text{Cr}_2\text{O}_7$. An analysis of a third grain from the type locality, by Dr. R.F. Symes of 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 $p_0 = 0.611$. Redledgeite is indeed class 4/m, but $p_0 = c$ 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 Mg₅Cr₂(SiO₄)₃.

**DISCUSSION**

Mannardite and redledgeite (as defined above) form the two end-members of an assumed solid-solution series, isosctructural at the subcell level, between (Ba⁺H₂O)(Ti₆V₃⁺)O₁₆ and (Ba⁺H₂O)(Ti₆Cr³⁺)O₁₆. Both minerals are of the cryptomelane or nonstoichiometric stuffed type, in which tunnel cations (Ba⁺) 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 (Ti⁶⁺V₃⁺Cr³⁺)O₁₆. 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 TiO₂], 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 Ba₂M₅ 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 Cr³⁺ or Fe³⁺ substitution within the M site at a semixed 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 is structural with priderite is observed. This persists to 5.30 Ti atoms, whereupon a monoclinic P2₁/m cell is structural 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.

**ACKNOWLEDGEMENTS**

This project would not have been possible without the able technical assistance of D.R. Owens, J.H.G. Laflamme and E.J. Murray of CANMET. The efforts of Dr. J.T. Szymański of CANMET in defining the redledgeite cell, on holotype material made available by Dr. I. Gray of CSIRO, are gratefully acknowledged; additional unpublished analytical data on a second specimen of redledgeite from the type locality were kindly provided by Dr. R.F. Symes of the British Museum (Natural History). A.J. Cridge of the British Museum (Natural History) performed the reflectance measurements on mannardite and contributed part of the section on optical properties. Dr. N.S. McIntyre of the University of Western Ontario analyzed the mineral by ion microprobe for its trace lithium content. We appreciate the support of Kidd Creek Mines Ltd., and acknowledge their permission to publish this paper. It is our personal memorial to George Mannard.
REFERENCES


Received July 12, 1984, revised manuscript accepted November 7, 1985. Delay caused by a new vote by the IMA Commission on New Minerals and Mineral Names on the validity and separateness of the two species.