

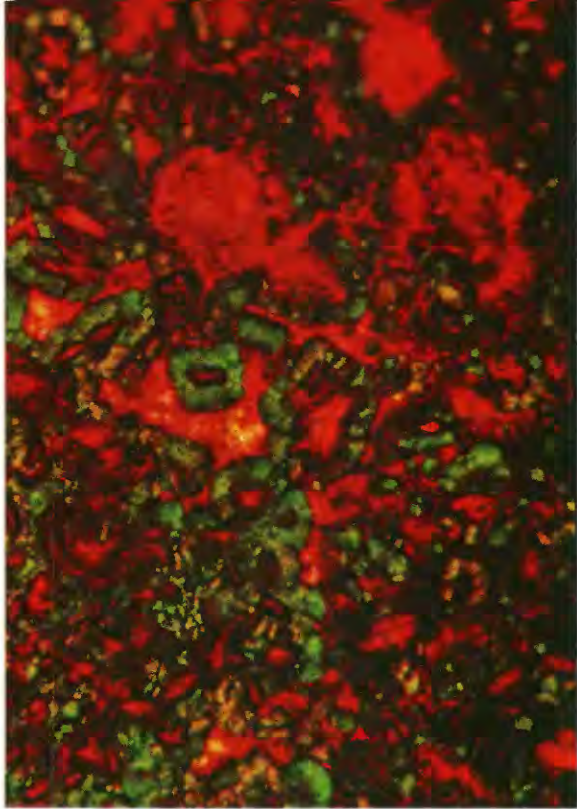
Merumite—A Complex Assemblage of Chromium Minerals from Guyana

GEOLOGICAL SURVEY PROFESSIONAL PAPER 887

*Prepared in cooperation with
the Geological Survey of Guyana*



**MERUMITE—A COMPLEX ASSEMBLAGE
OF CHROMIUM MINERALS FROM GUYANA**



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0.1 mm



0.1 mm



0.1 mm

Photomicrographs of four merumite thin sections illustrating the diversity of mineral composition and structure and the fineness of grain size. Plain transmitted light.

UPPER LEFT: Green eskolaite and red-brown guyanaite.

UPPER RIGHT: Banded structure of green eskolaite and yellow to brown guyanaite. The very bright polygonal area is a cross section of a quartz crystal.

LOWER LEFT: Reddish grimaldiite-mcconnellite aggregate filling opening in merumite specimen.

LOWER RIGHT: Green eskolaite and yellow-brown guyanaite showing banded structure.

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GEOLOGICAL SURVEY

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CONTENTS

	Page		Page
Abstract	1	Bracewellite, CrOOH—Continued	
Introduction and acknowledgments	1	Electron-probe study	16
Merumite	1	X-ray powder data	16
Nature and occurrence	1	Grimaldiite CrOOH and mcconnellite CrOOCu	17
Previous studies	6	Occurrence	17
Chemistry	7	Physical properties	18
Older analyses	7	Chemistry	18
Recent analyses	7	Electron-probe analysis	19
Isotopic study	7	X-ray data	19
X-ray powder data	7	Previous syntheses of rhombohedral CrOOH and	
Petrography	8	CrOOCu	19
Eskolaite	9	Relation of mcconnellite to delafossite	20
Occurrence in Finland and Guyana, and (possibly)		γ -CrOOH (synthetic)	21
Siberia	9	Synthesis	21
Chemistry	10	X-ray powder data and cell constants	22
Guyanaite	10	Chromian gahnite	22
Occurrence in Guyana and Finland, and synthesis	10	Properties	22
Chemistry	11	Electron-probe analysis	23
Analyses	11	X-ray data	23
Thermal behavior	12	Other chromian gahnites and zincian chromites	23
X-ray powder data	13	Chromian pyrophyllite	24
Bracewellite, CrOOH	13	Gold (and silver) in merumite	24
Occurrence and identification	13	Accessory minerals from Director Creek	24
Chemistry	15	Crystallographic relationships of CrOOH compounds ..	28
Analysis	15	References cited	28

ILLUSTRATIONS

[Plates follow references]

FRONTISPIECE. Photomicrographs of four merumite thin sections illustrating diversity of the mineral composition and structure and the fineness of grain size.

- PLATE**
1. Photographs of two very large merumite specimens.
 2. Photomicrographs of thin sections of merumite showing eskolaite and guyanaite.
 3. Photomicrographs of polished sections of merumite showing quartz, grimaldiite-mcconnellite polycrystals, and gold.
 4. Photomicrograph of bracewellite crystals and electron-probe analyses of two grimaldiite-mcconnellite polycrystals.
 5. Scanning-electron photomicrographs of grimaldiite-mcconnellite polycrystal and chromian gahnite crystals.
 6. Photomicrographs of fine-grained topaz aggregates.

	Page
FIGURE 1. Index maps showing location of merumite-bearing area in Guyana	3
2. Sketch map of Merume River area showing location of merumite deposit	4
3. Geologic map of Merume River valley	5
4. Graph of unit cell edge versus composition in natural and synthetic chromian gahnite	23

TABLES

	Page
TABLE 1. Older analyses of merumite	7
2. Recent analyses (in percent) of two specimens of merumite (eskolaite and guyanaite) from Guyana and of eskolaite from Finland	8

	Page
TABLE 3. Spectrographic analyses (in percent) of four merumite samples	9
4. X-ray powder patterns of merumite (eskolaite 37 percent, guyanaite 63 percent), merumite approaching eskolaite (Guyana), guyanaite (Guyana, four strongest lines), eskolaite (Finland), and Cr_2O_3	9
5. Cell constants of guyanaite (from Guyana and Finland), and of CrOOH , ScOOH , and InOOH	11
6. Analyses of guyanaite	12
7. X-ray powder data of $(\text{Cr, Al, Fe, Ti, Mn})\text{O}_2$ from guyanaite, and CrO_2 from CrOOH	13
8. X-ray powder data of $(\text{Cr, Al, Fe, Ti Mn})_2\text{O}_3$	13
9. X-ray powder data of guyanaite (from Guyana and Finland), "merumite" and synthetic guyanaite CrOOH	14
10. Analysis of merumite containing 70 percent bracewellite and 30 percent eskolaite	15
11. Spectrographic analysis of merumite containing 70 percent bracewellite and 30 percent eskolaite	15
12. Electron-probe analysis (in percent) of seven crystals of bracewellite and two merumite fragments	16
13. X-ray powder data for bracewellite, goethite, and eskolaite	17
14. Chemical analysis of grimaldiite-mcconnellite polycrystals	18
15. Microspectrographic analysis of grimaldiite-mcconnellite polycrystals	19
16. X-ray powder pattern of grimaldiite and mcconnellite	20
17. Cell constants of grimaldiite, mcconnellite, and related substances	21
18. X-ray powder patterns of $\gamma\text{-CrOOH}$ and lepidocrocite	22
19. Cell constants of $\gamma\text{-CrOOH}$ and related compounds	22
20. X-ray powder data for chromian gahnite $\text{Zn}(\text{Al}_{0.7}, \text{CrO}_{0.3})_2\text{O}_4$ from Guyana and synthetic spinels	23
21. Gold and silver in six fragments of merumite	24
22. X-ray powder data for topaz	25
23. Analysis of topaz	26
24. Crystallographic relationship of the CrOOH compounds and other metallic hydroxides	27

MERUMITE—A COMPLEX ASSEMBLAGE OF CHROMIUM MINERALS FROM GUYANA

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ABSTRACT

Merumite, found as black grains or pebbles in a small stream bed in Guyana, is a complex assemblage of hexagonal eskolaite (predominant), essentially Cr_2O_3 ; guyanaite and bracewellite, both orthorhombic and essentially CrOOH ; grimaldiite, rhombohedral and also essentially CrOOH ; and mcconnellite, rhombohedral CrOOCu , isostructural with grimaldiite and invariably intergrown with it. A spinel, chromian gahnite $\text{Zn}(\text{Al}_{0.7}\text{Cr}_{0.3})_2\text{O}_4$, chromian pyrophyllite, and free gold are present in very minor amounts. With the merumite is found a cryptocrystalline reddish or gray topaz, apparently found only here in Guyana. Quartz crystals present in merumite are evidently older than the merumite; the pyrophyllite is younger. Merumite is believed to be of hydrothermal origin.

Iron, aluminum, titanium, and vanadium replaced chromium in the merumite minerals.

INTRODUCTION AND ACKNOWLEDGMENTS

Merumite was discovered in 1937 in British Guiana (now Guyana) and was described by Bracewell (1946) as a new type of chromium ore, essentially a hydrated chromium oxide, with more than 80 percent Cr_2O_3 . In 1950, Michael Fleischer, U.S. Geological Survey, suggested to Charles Milton that merumite should receive further study. A preliminary examination of a few available specimens indicated a complex and highly varied composition; only after years of study by many investigators can it be said that the composition of merumite is now known. Field studies of the geology of the occurrence and laboratory investigations in the U.S. Geological Survey and at the George Washington University have clarified its geologic relations and probable origin and established its complex mineralogy. In the field, Sat Narain, Guyana Geological Survey, and Charles Milton, U.S. Geological Survey and George Washington University, have most recently studied the geology, following many previous expeditions of others. In the laboratory, microanalyses of various merumite minerals have been made by Blanche L. Ingram, Joseph I. Dinnin, and Frank Cuttitta, microprobe studies by Edward J.

Dwornik and Harry J. Rose, Jr., and crystallographic X-ray studies by Daniel Appleman, Margaret Hall Appleman, and Edward C. T. Chao. It should therefore be clear that this study of merumite was the work of a group, and no individual could have succeeded in unraveling the merumite enigma without the contributions of his coworkers. We are further indebted for the unfailing counsel of our colleague Michael Fleischer and for the generous assistance of Dr. R. B. McConnell and Dr. Sobharam Singh, formerly of the Guyana Geological Survey. Murray R. Director provided us with several excellent specimens of merumite described in this report. Dr. A. J. Tousimis, of Biodynamics Research Corporation, Rockville, Md., prepared the scanning electron photomicrographs in this report. Richard C. Erd, U.S. Geological Survey, has assisted generously in the task of reviewing the manuscript.

Milton and others (1968) referred to the new species guyanaite, bracewellite, grimaldiite, and mcconnellite; these new mineral names had been previously approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association.

Specimens of the merumite minerals have been deposited with the U.S. National Museum. An account of the geology of the merumite occurrence in Guyana has been published recently (Milton and Narain, 1969).

MERUMITE

NATURE AND OCCURRENCE

Merumite, discovered in 1937 in alluvial gravels in British Guiana, consists of black rounded grains, generally sand sized, although masses several centimetres across have been found; it was first described by Bracewell (1946) as a hydrated oxide of chro-

mium with some aluminum. Merumite was considered to be a mineral species until Milton and Chao (1958) reported that eskolaite, Cr_2O_3 , discovered in a Finnish base-metal ore by Kouvo and Vuorelainen (1958), was a major constituent, along with other unidentified chromium minerals. From the present study, merumite is known to contain at least seven chromium minerals, only three of which, eskolaite, guyanaite, and chromian pyrophyllite, have been found elsewhere in the world (but only in two localities). Except for bracewellite, all the chromium compounds discovered in merumite have been made in the laboratory.

Although the term merumite is no longer applicable as a mineral name, it should be retained to designate the complex assemblage of minerals described in this report. Its characteristic appearance and properties easily differentiate it from other hard black opaque substances found in nature. It may be defined as a fine-grained to aphanitic aggregate of (mainly) chromium oxide (eskolaite), three hydrous chromium oxides (guyanaite, bracewellite, and grimaldiite), a copper-chromium oxide (mcconnellite), a chromian zinc aluminum spinel (chromian gahnite), with quartz, gold, and chromian pyrophyllite; all of these may not be present in all specimens.

Merumite has a very characteristic appearance, and once seen, it is not likely to be mistaken. Its specific gravity (about 4.5), hardness (about 5 to 9), shining black color, rounded contours (often seen on specimens which appear to be fragments of larger masses), imprint of prismatic quartz crystals (which rarely may still be embedded in merumite), and generally green (rarely brown) streak are all diagnostic.

Plate 1 shows the exterior and sawed interior surfaces of two unusually large specimens of merumite. The botryoidal exterior and quartz crystal inclusions (see also pl. 3, fig. 1) are characteristic. Granular aggregates of grimaldiite-mcconnellite polycrystals can also be seen in plate 1, figure 4, as dark mottled areas, less than 1 cm across, near the center of the specimen.

The presence in merumite of free gold, pyrophyllite rosettes, and doubly terminated quartz crystals suggests that merumite was formed in a hydrothermal type of deposit. None of the minerals associated with merumite in the placer gravels contains chromium, and only the coarse euhedral quartz, pyrophyllite, and possibly jasper and unusual types of topaz found with, but not in, merumite, may be genetically related. The hydrothermal merumite,

carrying pyrophyllite and gold, and perhaps the topaz may have been deposited in the easily decomposed Roraima(?) sandstone-ash series, of which Robello Ridge may be an outlier and which may have since disappeared by erosion; the resistant merumite and topaz became concentrated, eventually, in Director Creek.¹ Large beds of volcanic ash, more or less silicified and carrying euhedral quartz and jasper, are contiguous to the merumite placer gravels, but have no known chromium mineralization.

Merumite is found most abundantly in the upper branches of Director Creek, a small tributary of the Merume River which in turn flows into the Mazaruni River (fig. 1). The nearest inhabited place is Kamakusa, a government rest house and hydroplane stop on the Mazaruni River, about long 60° W., lat 6° N. The merumite area is about 16 km (10 miles) southwest of Kamakusa but, because of the windings of the rivers, the trip takes several hours by motorboat. The Merume River is generally navigable by small boats up to the First Falls, except in periods of very low water or of very high water when the current is dangerously swift. The location of the merumite deposit in the Merume River valley is shown in figure 2.

The largest concentration of merumite is in a strip 3.0–4.5 m (10–15 feet) wide and about 3 km (2 miles) long at the base of Robello Ridge², which consists of Roraima-like sandstones, conglomerates, and volcanic ash, with dips of 30° to the east (fig. 3). Shale, jaspilite, quartzite, and tuff of the Haimaraka Formation are exposed in the river to the west of the ridge. To the east of Robello Ridge, a large area of agglomerate was reported by Matthews³. Ten to eleven kilometres (6–7 miles) west, dolerite (diabase) intrudes the scarp-forming Roraima Formation.

The merumite deposit is in low-lying swampy and forested terrain, about 80 m (260 feet) above sea level; sand terraces (White Sand Formation) rise some 15 m (50 feet) higher. A few miles to the east, west, and south are scarps of the Roraima Formation with extensive talus slopes; the scarps reach altitudes of 915 m (3,000 feet) above sea level. The Merume River and its major tributaries rise on the Pakaraima Plateau above the escarpment. Below the First Falls, the river flows through a swampy forested plain before joining the Mazaruni

¹ Named for Murray R. Director, who examined the merumite deposit in 1957.

² Named for Joseph Robello of Georgetown, Guyana, who prospected the area for diamonds and merumite, and who was helpful in locating the deposit.

³ P. F. P. Matthews, November 18, 1953, Report of merumite for African Manganese Co., Ltd.; 5-page typescript and map on file in office of Guyana Geological Survey, Georgetown.

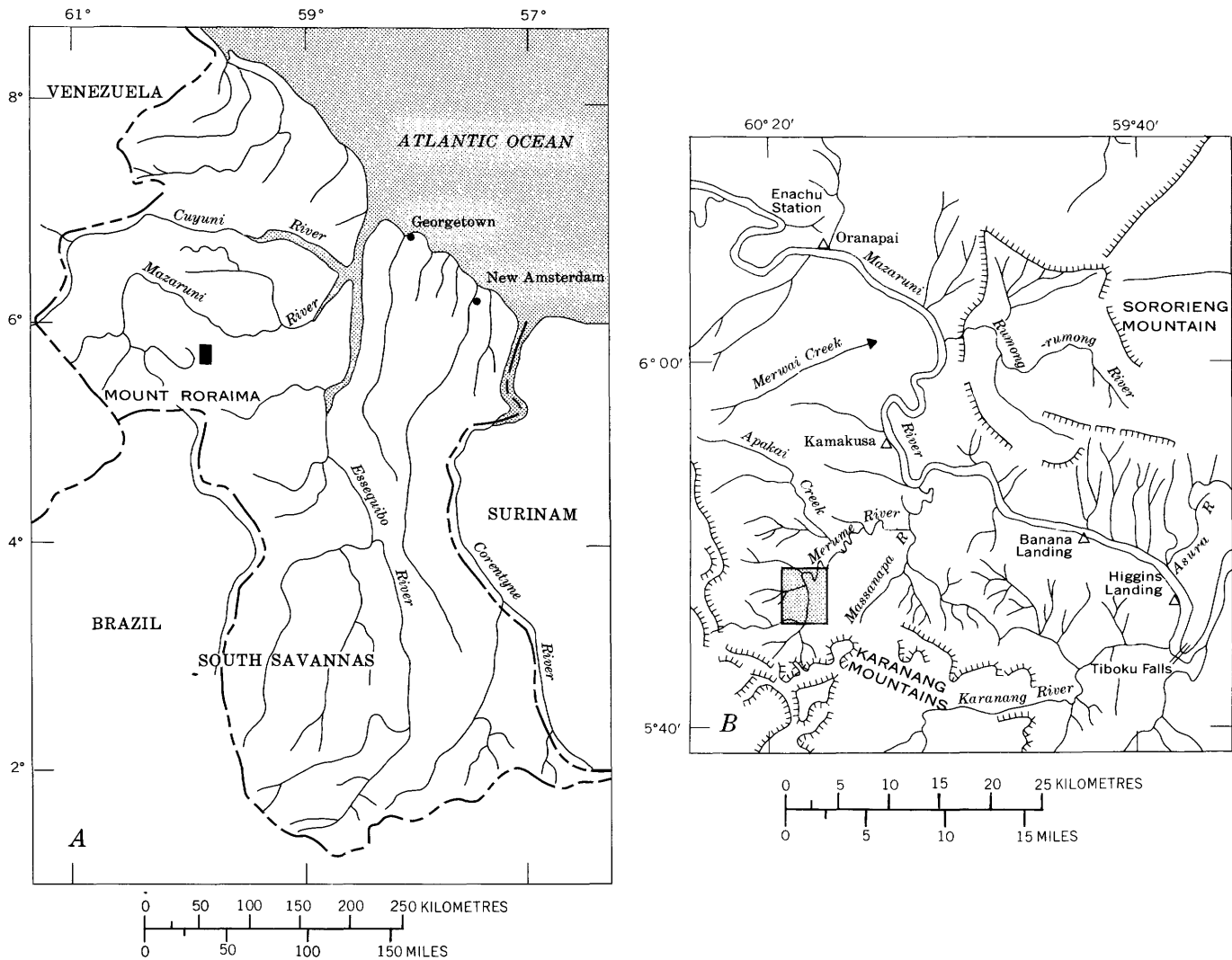


FIGURE 1.—Index maps showing A, location of merumite-bearing area (shaded) in Guyana, and B, enlarged view of merumite-bearing area (shaded) and surrounding region. Merumite-bearing area is shown in greater detail on figure 2. Escarpments are shown in B by hachured lines.

River. Eight kilometres (5 miles) north of the escarpment, and immediately above First Falls, the Merume River runs northwards along the western side of Robello Ridge, which rises about 92 m (300 feet) above the river.

In addition to the major concentration at the base of Robello Ridge, a small amount of merumite was found at the edge of a White Sand plateau near the point where Gordon Creek joins the Merume River. Gordon Creek itself was prospected, and a few pieces were found on the right bank, approximately 0.8 km (0.5 mile) and 1.6 km (1.0 mile) upstream from its mouth. A few pieces were found in Copper Creek, which flows into the Merume River a short distance above Third Falls. Merumite was also found in many of the small creeks flowing along the east

side of Robello Ridge for a distance of 2.4 km (1.5 miles). Merumite has been reported in the Merume River, immediately above White Creek, in a diamondiferous gravel overlain by 1.8–2.4 m (6–8 feet) of alluvial sand.

Merumite is recovered from the gravels by the same methods used in recovering alluvial diamonds and gold. Dredging, with or without suction, is feasible in the river gravels. Where the merumite gravels underlie forest growth, as at the base of Robello Ridge, arduous clearing of the trees and matted roots is necessary. The gravel is washed in Brazilian sieves ($\frac{3}{8}$ -, $\frac{1}{4}$ -, and $\frac{1}{8}$ -inch mesh), and the merumite is picked off the two coarser sieves. The fine concentrate on the $\frac{1}{8}$ -inch-mesh sieve is set aside for washing on a steel batelle. Rarely, small dia-

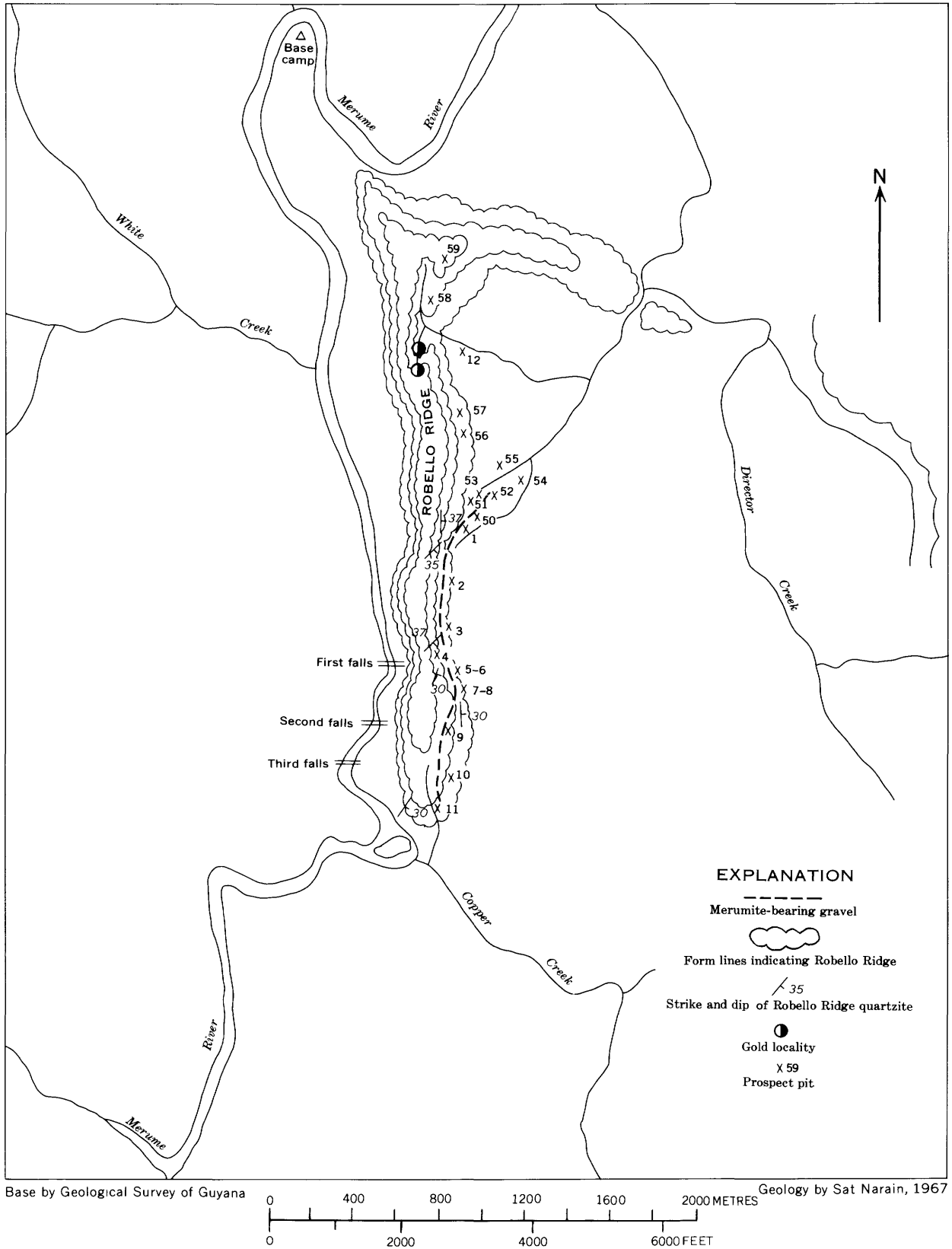












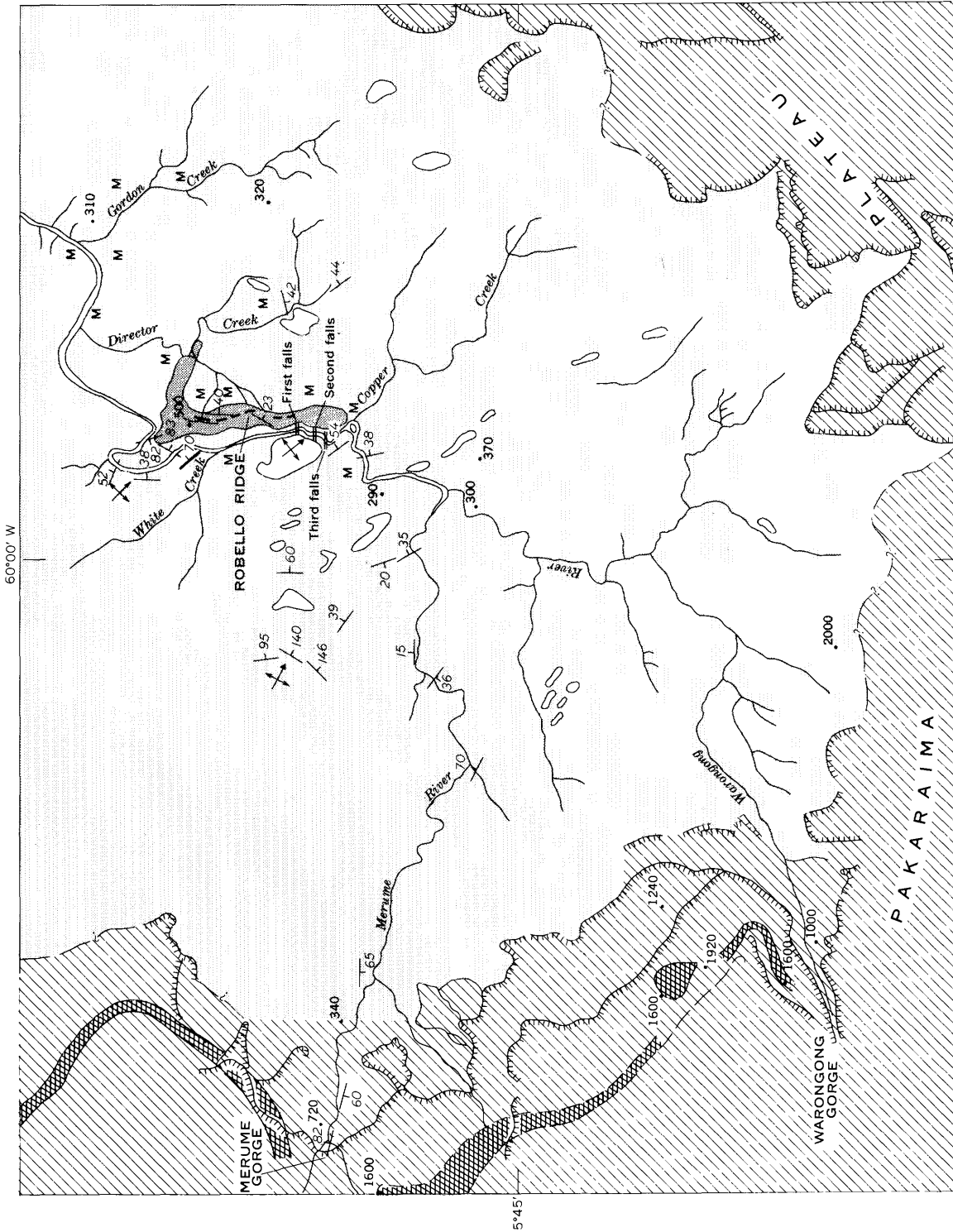


FIGURE 2.—Sketch map of the Merume River area showing the location of the merumite deposit. Area of this map is shaded on figure 1.

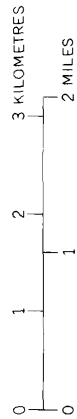
MERUMITE

EXPLANATION

-  Roraima Formation (Paleozoic?), Current-bedded sandstone
-  Pink quartzites of Robello Ridge
-  Haimaraka Formation (Precambrian?), Purple phyllites, conglomerate, and sandstone beds
-  Dolerite (Mesozoic?), Younger mafic intrusives
-  Strike and dip of beds
-  Fault, showing dip
-  Anticline, showing fold axis and direction of plunge
-  Escarpment
-  Concentration of merumite deposit
-  Low hills
-  Feet above sea level
-  Merumite occurrence



Geology modified from M.G. Aldridge, 1959 and 1962. Data on merumite deposit from Sat Narain, 1971. Reports on file with the Geological Survey of Guyana



Base by Geological Survey of Guyana

FIGURE 3.—Geologic map of the Merume River valley showing Robello Ridge and merumite localities.

monds or gold nuggets have been found on the batelle. The general recovery of merumite from the Robello Ridge gravels is about 110 g/m³. The depth to the merumite-bearing gravel varies from 20–46 cm (8 to 18 inches) and the thickness of the gravel from 15–30 cm (6 to 12 inches). The gravel consists essentially of quartz crystals and milky quartz, with red jaspilite, a little topaz (of an unusual chertlike type) and brown rutile crystals with other minerals, described below, and water-worn fragments of white or pink sandstone and volcanic ash in a red clayey sand. The clayey sand, quartz, and jaspilite are derived from the sandstone of Robello Ridge. Rounded pebbles of basaltic rock and dark pebbles of a widespread quartz-tourmaline hornfels (“carbon”) are found with the merumite and are a possible source of confusion to the inexperienced prospector. The small rutile crystals are sometimes termed “tin” by the miners, but the presence of cassiterite is very doubtful. Gorceixite has been reported, but actually it may have been topaz. However, cassiterite and gorceixite do occur elsewhere in Guyana.

The fact that the occurrence of merumite is limited to the small area shown on the maps implies a local origin, and the relative concentration along the base of Robello Ridge indicates that the rocks of the ridge may have a genetic relationship to merumite. The ridge rocks show mild hydrothermal metamorphism, the sandstones containing euhedral quartz crystals in vugs, similar to those found with the merumite. The ash beds are locally silicified, having bands of red jaspilite also similar to the pebbles found with merumite.

The generally rounded, often polished, shapes in which merumite is found suggests mechanical attrition and thus a history of travel. No pyrophyllite or gold has been seen on the surface of any specimen of merumite; even quartz is usually completely removed. Nevertheless, the distance of travel cannot have been great because merumite is found only in a limited area, and because the largest known specimens weigh many ounces. Even so, the apparent attrition seems hard to reconcile with the considerable hardness of merumite, or at least of eskolaite, one of the major components. Likewise, the appearance of fracturing is not easy to explain for material as hard and tough as most merumite. Perhaps the merumite was both softer and more easily broken when first formed than it is now, and hardness and toughness result from recrystallization or possibly weathering.

The statement of Ramdohr (1960, p. 870) that

merumite is certainly a weathering product of chromite cannot be verified. He observed that its genesis is obscure, but our observations strongly imply a hydrothermal origin. No chromite is known in the Merume River valley. Ramdohr further (p. 884) noted with surprise (“überraschend”) the report by Milton and Chao (1958) of the occurrence of eskolaite in merumite, as he (erroneously, in our opinion) views merumite as a weathering product of chromite (p. 870). Recently (written commun., July 3, 1968) he refers to eskolaite as “by far the most important component of merumite.” While this may be true for the particular specimen or specimens which he examined, guyanaite appears to be at least equally abundant generally.

Ramdohr (1969) referred to merumite only to note that it has been reported to contain eskolaite (p. 945). The eskolaite, from the Outokumpu Mine in Finland is described in detail; no reference to the other merumite minerals is made.

A detailed report on the history and geology of merumite (Milton and Narain, 1969) summarizes the work of many geologists in Guyana.

Vuorelainen and others (1968) described guyanaite (but did not name it) from the Outokumpu mine in Finland as an alteration product of eskolaite; both are found in sulfide-rich apophyses of the main ore body which occur in skarn-bearing quartzite dikes emplaced after strong tectonic movements. Besides sulfides and eskolaite with guyanaite, zincian chromite, rutile, uraninite, nolanite, corundum, titanite, zircon, and graphite are present in the ore body. Fuchsite (chromian muscovite) coats some eskolaite—guyanaite crystals. From the description by Vuorelainen and others (1968), it appears that the eskolaite-guyanaite alteration is hydrothermal, and not a weathering product. Although eskolaite with guyanaite is found in the Outokumpu deposit, nothing like merumite is known from there.

PREVIOUS STUDIES

After the initial recognition of merumite by Bracewell (1946), scattered and fragmental data appeared, most of them erroneous to some extent. They are noted and commented upon in appropriate places in this report. The reason for the invalidity of earlier studies was nonrecognition of the complexity and diversity of all merumite specimens, their superficial similarity notwithstanding. In this study, many hundreds of specimens have been examined. Two areas in which little work has been done are the microscopic petrography of merumite in thin and polished sections and the physical chem-

istry, particularly phase relations, of its constituent minerals.

CHEMISTRY

OLDER ANALYSES

Two published analyses (Bracewell, 1946) and one unpublished analysis (made in 1956–57) of merumite are given in table 1. The first two were of specimens with green and brown streaks respectively, which could indicate either variation in mineral content or the (recognized later) variability in color of gyanaitite. Without mineralogical data, the value of these analyses is limited; nevertheless, they do show the typical and restricted range in composition of what may be presumed to be average samples.

RECENT ANALYSES

Analyses made by the U.S. Geological Survey include a merumite containing 37 percent eskolaite and 63 percent gyanaitite (table 2) and one containing 70 percent bracewellite and 30 percent eskolaite (tables 10 and 11); these analyses include spectrographic data. Table 2 also includes spectrographic data for a merumite containing more gyanaitite than eskolaite (analysis D), and, for comparison, the analysis of eskolaite from Finland (Kouvo and Vuorelainen, 1958). Spectrographic analyses of four merumite samples of undetermined mineral composition are given in table 3; these samples were assayed for gold and silver (table 21). It

is not likely that any further analyses will be made of merumite, now that it is known to be a mixture of many minerals.

The role of Al_2O_3 , Fe_2O_3 , TiO_2 , Mn_2O_3 , and V_2O_5 , which generally appear in the chemical analyses of merumite and its constituent minerals, is one of general partial substitution for the dominant Cr_2O_3 . There are indeed, as will be seen, specific minerals characterized by major Al_2O_3 : chromian pyrophyllite, chromian gahnite, and topaz. However the first and second are of sporadic and quantitatively negligible occurrence in merumite, and the third accompanies but has never been found in merumite. Chemical analyses of merumite and of the constituent oxide-hydroxide minerals were all made on material apparently free from these three Al_2O_3 -containing minerals.

ISOTOPIC STUDY

Svec and others (1962) studied the relative abundance of the chromium isotopes Cr^{50} , Cr^{52} , Cr^{53} , and Cr^{54} in a large number of terrestrial and meteoritic chromium minerals, including a sample of merumite, and found no evidence of any significant isotopic variation in any of their specimens.

X-RAY POWDER DATA

Because merumite is a mixture (although, rarely, almost monomineralic), X-ray powder patterns are basically composites to be resolved as patterns of the component minerals.

Unless otherwise noted, the X-ray powder diffraction patterns of this report were obtained on a standard 114.6 mm. camera, using Ni-filtered Cu radiation. Since the objectives of this report are primarily the identification of unknown phases present, rather than precise measurements of known phases, methods of obtaining high precision, (for example, internal standards) were not used. For similar reasons, letter scales, such as vs, s, w, and so forth, rather than numerical values which imply high precision, were used in the tables.

Table 4 gives powder patterns for merumite (eskolaite 37 percent, gyanaitite 63 percent), for merumite approaching eskolaite in composition, for gyanaitite from Guyana (four strongest lines only), for eskolaite from Finland, and for Cr_2O_3 .

Table 9 gives powder patterns of two merumites which are almost wholly gyanaitite (although one has a little eskolaite and quartz), of pure gyanaitite crystals from Guyana and Finland, and of synthetic gyanaitite.

TABLE 1.—Older analyses of merumite

[n.d., looked for but not detected]

Constituents	Analyses (in percent)		
	A ¹	B ²	C ³
Cr_2O_3 -----	81.30	76.74	80.28
Al_2O_3 -----	6.55	6.82	----
Fe_2O_3 (total Fe) -----	1.58	5.91	2.10
TiO_2 -----	.75	1.40	----
V_2O_5 -----	.15	.15	----
MnO -----	.06	.06	----
H_2O^- -----	.10	.11	----
H_2O^+ -----	8.08	8.25	----
SiO_2 -----	1.30	.95	1.78
MgO -----	n.d.	n.d.	----
S -----	----	----	.36
P -----	n.d.	n.d.	trace
Ca, Ba, Zr, Ni, Nb, Ta --	n.d.	n.d.	----
Total -----	99.87	100.39	84.52
Specific gravity -----	4.49	4.44	----

¹ Analyst, W. H. Bennett, Imperial Institute, London (Bracewell, 1946). Bracewell reported a green streak; Stockley (1955) gave the same analysis but erroneously reported the streak as brown (Bennett, oral commun., 1969).

² Analyst, W. H. Bennett, Imperial Institute, London (Stockley, 1955). Stockley reported a green streak, but this is erroneous; the original report was "brown streak" (Bennett, oral commun., 1969). Stockley omitted the specific gravity, which was determined by Bennett.

³ Analyst Andrews S. McCreath and Son, Harrisburg, Pa. (Murray Director, written commun., 1957)

TABLE 2.—Recent analyses of two specimens of merumite (eskolaite and guyanaite) from Guyana and of eskolaite from Finland

Constituent	Amount (in percent)
MERUMITE¹ (ESKOLAITE, 37 PERCENT; GUYANAITE, 63 PERCENT) ANALYSIS A²	
Cr ₂ O ₃ -----	88.8
Al ₂ O ₃ -----	3.1
CaO -----	.1
H ₂ O -----	2.3
Ignition loss -----	(3.5)
Total -----	94.3
ANALYSIS B³	
Cr ₂ O ₃ -----	89.2
ANALYSIS C⁴	
Si -----	0.02
Al -----	1.5
Fe -----	.1
Mg -----	.01
Ca -----	.1
Ti -----	.015
Mn -----	.03
Ag -----	.001
As -----	.2
Au -----	.07
Be -----	.0015
Cu -----	.02
Ga -----	.001
Mo -----	.015
Nb -----	.03
Ni -----	.002
Pb -----	.01
Sb -----	.2
Sr -----	.002
V -----	.15

¹ This specimen was analyzed to test analytical procedures for similar quantities.

² Analyst, J. I. Dinnin, U.S. Geological Survey. Sample massive, black; X-ray film 16827 (table 4). Water and ignition loss were determined by ignition of a 100-mg sample in a microcombustion tube swept with argon; the increase in weight of an absorption tube packed with Anhydron represented the water content of the sample and the loss in weight of a quartz combustion boat containing the sample represented the ignition loss. The ignited sample was dissolved in perchloric acid and used for the determination of chromium by oxidation with ammonium persulfate-silver, reduction with ferrous ammonium sulfate, and titration with potassium dichromate solution. A 50-mg sample was dissolved in perchloric acid, electrolyzed in a mercury cathode apparatus, and diluted with water. An aliquot was used for the determination of calcium by flame photometry.

For discussion of the low summation, see section on thermal behavior of synthetic guyanaite. Computation of mineral composition of this merumite varies with unknown factors, such as the true percentage of H₂O and the distribution of Al₂O₃, and so forth, between eskolaite and guyanaite. With 6.8 percent H₂O (the maximum derived from 89.2 percent Cr₂O₃ and 4.0 percent Al₂O₃, and so forth) and all Al₂O₃, and so forth, in guyanaite, a composition of 38 percent eskolaite and 62 percent guyanaite follows; and with all Al₂O₃, and so forth, in eskolaite, 36 and 64 percent respectively; the mean is then eskolaite 37 and guyanaite 63 percent.

Table 13 gives patterns of two merumite samples, both almost wholly bracewellite but having a little guyanaite.

PETROGRAPHY

Efforts over many years to prepare standard thin sections of merumite were invariably unsuccessful, because the intense absorption of most of the merumite minerals necessitated unusually thin sections to transmit light, but the almost invariable presence of the very hard eskolaite (H=9.5) associated with the much softer minerals made such thin sections

TABLE 2.—Recent analyses of two specimens of merumite (eskolaite and guyanaite) from Guyana and of eskolaite from Finland—Continued

Constituent	Amount (in percent)
ANALYSIS C¹ (SPECTROGRAPHIC) MERUMITE¹ (ESKOLAITE, 37 PERCENT; GUYANAITE, 63 PERCENT—Continued ANALYSIS C¹—Continued	
K, P, B, Bi, Cd, Ce, Co, Ge, Hf, Hg, In, La, Li, Pd, Pt, Re, Sc, Sn, Ta, Te, Th, Ti, U, W, Y, Yb, Zn, Zr.	Looked for but not detected.
MERUMITE (GUYANAITE PLUS ESKOLAITE) ANALYSIS D² (SPECTROGRAPHIC)	
Cr -----	>25
Al -----	1-9
Si, Fe, Ti, V -----	0.X
Mg, Mn, Ca, Cu, Ge, Sb -----	0.0X
Pb, Mo, Be -----	0.00X
Ag, Sn, As, Bi, Tl, Co, Ni, Zn, Cd, Zr, B, P, Ba, Sr, Y, La, U, Th, Cb, W, Pt, Au.	Looked for but not detected.
ESKOLAITE ANALYSIS E³	
Cr ₂ O ₃ -----	94.13±0.20
Al ₂ O ₃ -----	⁷ 0.19
Fe ₂ O ₃ -----	0.55
V ₂ O ₅ -----	4.58
MgO -----	⁷ 0.03
MnO -----	⁷ 0.03
SiO ₂ -----	⁷ 0.20
H ₂ O -----	0.10
Total -----	⁸ 99.81
Density -----	5.18 measured 5.218 calculated.

² Analysts, H. J. Rose and Frank Cuttitta, U.S. Geological Survey. Average of three determinations made by X-ray fluorescence analysis. A solution-pellet technique was used to prepare the samples and the K₂Cr₂O₇ standards.

Weight sample (in mg)	Cr ₂ O ₃ (percent)
1.98 -----	89.1
2.47 -----	89.4
2.47 -----	89.2

⁴ Spectrographic analysis by Helen Worthing, U.S. Geological Survey. As to the reliability of the determinations, results are reported in percent to the nearest number in the series 1, 0.7, 0.5, 0.3, 0.2, 0.15, 0.1, and so forth, which represent approximate midpoints of interval data on a geometric scale. The assigned interval for semiquantitative results will include the quantitative value about 30 percent of the time.

⁵ Spectrographic analysis by K. J. Murata, U.S. Geological Survey. X-ray film 4864. This was a different sample from the one later analyzed by Dinnin, Rose and Cuttitta, and Worthing (A, B, and C, respectively) and was analyzed to identify a (then) new and strange X-ray powder pattern.

⁶ Analyst, Jorma Kinnunen, in Kouvo and Vuorelainen (1958) who gave the formula, Cr_{11.90}V_{0.05}Fe_{0.05}O₃.

⁷ Based on spectrographic analysis.

⁸ Spectrographic analysis also showed traces of Cu and Ni.

impossible to prepare. However, the edges of a few sections were sufficiently translucent to reveal some textural and mineralogical detail, but, even then, very intense illumination, painful to the eye, was required. Since those earlier attempts, however, modern methods using diamond abrasives and suitable polishing agents have produced good, sufficiently thin, sections as well as polished surfaces for study in reflected light.

The frontispiece shows the appearance of some specimens of merumite under transmitted light. Although merumite consists of a small number of min-

TABLE 3.—Spectrographic analyses (in percent) of four merumite samples^{1, 2}
[G. W. Sears, Jr., U.S. Geological Survey, analyst]

Percent	Analyses			
	A	B	C	D
(>10)	Cr	Cr	Cr	Cr
7	Al			
5		Al, Fe	Al	Al, Fe
3		Ti	Fe, Ti	
2				Ti
1.5				
.7	Fe			
.3	V	Si, V	Si, V	Si, V
.15	Si, Ca, Cu	Ca, Sb, Mn	Mn, Cu	Ca, Zn, Mn
.1	Ti	Cu	Ca, Sb	Sb, Cu
<.1	Ce	Ce	Ce	Ce
<.05	Zn			
.03	Sb, Mg, Au	Nb	Nb	Pb
.02	Mn	Pb		Mg
<.02		Zn	Zn	
.015	Ni	Ni, Ga, Ge	Ni, Pb, Mg	Ni, Ge
.01	Pb, Ga, Mo	Mg	Ga, Ge	Ga, Nb, Zr
.007	Ba, Co, Ge	Mo, Zr	Ba, Mo, Zr	Mo
.005	Sr	Ba, Sr		Ba, Sr
<.005		Co	Co	Co
.003	Ag, Be		Sr	
.002		Be	Be, Sn	Be
.0015	Zr	Sn		Sn
.0007	Sc	Sc	Sc	Sc
.0005				Sc
Looked for but not found.	K, P, As, B, Bi, Cd, Hf, Hg, In, La, Li, Nb, Pb, Pt, Re, Sn, Ta, Te, Th, Tl, U, W, Y.	K, P, Ag, As, Au, B, Bi, Cd, In, La, Li, Pd, Pt, Re, Ta, Te, Th, Tl, U, W, Y.	K, P, Ag, As, Au, B, Bi, Cd, Hf, Hg, In, La, Li, Pd, Pt, Re, Ta, Te, Th, Tl, U, W, Y.	K, P, Ag, As, Au, B, Bi, Cd, Hf, Hg, In, La, Li, Pd, Pt, Re, Ta, Te, Th, Tl, U, W, Y.
Not looked for	Na, Yb	Na, Yb	Na, Yb	Na, Yb

¹“Results are reported in percent to the nearest number in the series, 1, 0.7, 0.5, 0.3, 0.2, 0.15, and 0.1, etc., which represent approximate mid-points of interval data on a geometric scale. The assigned interval for semiquantitative results will include the quantitative value about 30 percent of the time.”
² Assayed for gold and silver, see table 21.

erals, their relative amounts, crystal habits, and relationships to one another vary greatly from specimen to specimen, and almost every thin section

shows some features of special interest. None of the minerals of merumite shows alteration or weathering, although the merumite itself is characteristically rounded.

ESKOLAITE

OCCURRENCE IN FINLAND AND GUYANA, AND (POSSIBLY) SIBERIA

Eskolaite, essentially Cr₂O₃, was discovered by Kouvo and Vuorelainen (1958) in a base-metal skarn in the Outokumpu mine, Finland, and by Milton and Chao (1958) in merumite in Guyana. The parageneses of the two occurrences of eskolaite are completely different. In Outokumpu, well-crystallized eskolaite is a very minor constituent in the varied rocks and ore, but in Guyana, it is a major constituent of merumite. No good crystals of eskolaite have been seen in merumite, only massive aggregates which rarely show obscure crystal faces on botryoidal surfaces in vugs (pl. 2, fig. 1). In thin sections, zoning of the eskolaite is seen locally in bands varying from green to nearly black (pl. 2, fig. 2).

Such aggregate of eskolaite may (not commonly, however) be fairly free from admixed minerals, so that the X-ray powder pattern shows only eskolaite lines. One such pattern is given in table 4 (second analysis) with, for comparison, patterns of eskolaite from Finland (fourth analysis), and of Cr₂O₃ (fifth analysis). The same table also gives (first anal-

TABLE 4.—X-ray powder patterns of merumite (eskolaite 37 percent, guyanaite 63 percent), eskolaite (Guyana) guyanaite (Guyana), eskolaite (Finland), and Cr₂O₃

Merumite, film 16827 ¹		Merumite approaching eskolaite, film 16765 Guyana		Guyanaite, film 00188 Guyana (four strongest lines)		Eskolaite, Finland (Kouvo and Vuorelainen, 1958)			Cr ₂ O ₃ XPDF 6-0504 ²		
I ³	d	I ³	d	I ³	d	I	d	hkl	I	d	hkl
s	3.633	vs	3,601			96	3.63	-----	74	3.633	012
vwb	3.433										
w	G 3.220			vvs	3.224						
vs	2.663	vs	2.652			97	2.665	-----	100	2.666	104
vs	2.478	w	2.468			94	2.479	-----	96	2.480	110
vw	G 2.4395			vs	2.432						
vvw	2.206					5	2.269	-----	12	2.264	006
s	2.176	w	2.168			50	2.174	-----	38	2.176	113
									9	2.048	202
s	1.814	w	1.807			60	1.8146	-----	39	1.8156	024
vs	1.672	s	1.666			100	1.6746	-----	90	1.672	116
vw	G 1.641			s	1.636						
						5	1.6139	018			
vvw	G 1.608			ms	1.609						
vvw	1.581					5	1.5782	-----	13	1.579	122
s	1.464	vw	1.460			30	1.4656	-----	25	1.465	214
s	1.431	w	1.426			45	1.4331	-----	40	1.4314	300
wwb	1.296	vvw	1.30			12	1.2971	-----	20	1.296	10.10
wwb	1.240					5	1.2440	-----	17	1.2398	220

¹ For analysis, see table 2.
² X.P.D.F. 6-0504 refers to Index (Inorganic) to the Powder Diffraction File 1972, Joint Committee on Powder Diffraction Standards, Swarthmore, Penn.
³ vvs, very very strong; vs, very strong; s, strong; ms, medium strong; w, weak; vw, very weak; vvw, very very weak; b, broad line; G, guyanaite line.

ysis) the pattern of a merumite specimen which is mainly (37 percent) eskolaite.

The occurrence of eskolaite in Guyana is described in the section on "Nature and occurrence," of merumite. The Outokumpu mine in Finland is worked for its copper content, estimated to be about a million tons, but seven times as much chromium is present in serpentine and skarn rocks. Eskolaite, in large black (very dark green in transmitted light) prismatic to platy euhedral crystals, is found in the mine in several associations summarized by Kouvo and Vuorelainen (1958, p. 1100) as follows:

1. Chromium-bearing tremolite, skarn, rich in calcite, from contact with ore. Mineral habit: long hexagonal prisms (up to 5 mm). Associated minerals: pyrrhotite, pentlandite, chalcopyrite, chromium-bearing tremolite, uvarovite, tawmawite, calcite, and talc.
2. Quartzite from the foot wall of the ore. The specimen is from a cavity in a vein of milky quartz. Mineral habit: long prismatic (up to 1.5 mm). Associated minerals: uvarovite, chromium-bearing tremolite, calcite, and pyrite (pentagonal dodecahedron).
3. Veins of pyrrhotite. Mineral habit: platy (up to 6–7 mm). Associated minerals: pyrrhotite, chromium-bearing tremolite, and chromium tourmaline. In some cases the mineral occurs as thin sheets on the surface of quartz.
4. Skarn ore rich in pyrrhotite. Mineral habit: short prismatic. Associated minerals: chromium-bearing tremolite, uvarovite, chromium tourmaline, chromium spinel, pyrrhotite, pyrite (octahedron), and chalcopyrite.
5. Chlorite seams. Mineral habit: thin platy. Associated minerals: chlorite, pyrite, chalcopyrite, pyrrhotite, and chromium spinel.

The mineral has not been found to occur with chromium diopside.

The "chromium spinel" is chromite of very unusual composition, containing 5.8 percent zinc (Thayer and others, 1964).

The association in Finland of eskolaite with copper and zinc sulfides and zincian chromite may be compared with the presence in merumite of copper (in mcconnellite) and zinc (in chromian gahnite).

Ramdohr (1960, p. 332) suggested that an unidentified extremely hard mineral found in native platinum from Nizhne Tagilsk, Ural Mountains, Siberia, may be eskolaite. Ramdohr (1969, p. 944–945) gives a detailed account of (Finnish) eskolaite, and suggests that fine unmixing products in chromite or chromium spinel may be eskolaite rather than, as generally held, hematite.

CHEMISTRY

Unlike the eskolaite from Finland, pure eskolaite from Guyana has never been found in crystals large enough even for microanalysis. Single crystals of guyanaite and other merumite minerals, except eskolaite, are found only in rare microscopic vugs

or fissures in merumite. Before it was realized that merumite is a complex assemblage of minerals, numerous analyses were made (prior to 1950) under the mistaken idea that a single definite mineral was being analyzed. More recently, however, aware from optical and X-ray study that we were dealing with relatively simple mixtures, we have made further analyses of merumite, because microanalytical procedures for such small quantities of pure minerals were not known and experimentation on the few milligrams of isolated pure minerals obtained laboriously through months or years of toil would have been hazardous, if not reckless. However, on samples of several hundred milligrams of known complex composition (as determined by X-ray and optical studies) experimentation was permissible, and valid analytical methods were worked out which were later applied to microquantities of the handpicked pure crystals.

The Finnish eskolaite (table 2, analysis E) is 94 percent Cr_2O_3 ; almost all of the remaining 6 percent is V_2O_5 of very similar molecular weight. The Guyana eskolaite, however, may vary from almost wholly Cr_2O_3 with very minor Al_2O_3 (table 2, analysis A) in a specimen with guyanaite to a theoretical composition with more $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ ($(\text{Cr}_{0.25}\text{Fe}_{0.44}\text{Al}_{0.29}\text{Ti}_{0.00}\text{V}_{0.02})_2\text{O}_3$; see table 10) than Cr_2O_3 in a specimen with major (70 percent) bracewellite.

Spectrographic analysis of a merumite specimen with more (according to the X-ray powder pattern) guyanaite than eskolaite and, for comparison, the analysis (not spectrographic) of the Finnish eskolaite are given in table 2. The Finnish eskolaite has a reported density of 5.218 (powder data) or 5.20 (single-crystal data); pure Cr_2O_3 has a density of 5.25 (Kouvo and Vuorelainen, 1958, table 3, p. 1,104). Computation of the density of eskolaite in an analyzed specimen (table 10) of merumite containing approximately 70 percent bracewellite and 30 percent eskolaite gives values ranging from 4.86 to 5.21 with a mean of 5.035 ± 0.1755 .

GUYANAITE

OCCURRENCE IN GUYANA AND FINLAND, AND SYNTHESIS

Tombs and others (1964) synthesized orthorhombic CrOOH with unit cell dimensions $a=4.861$ Å, $b=4.292$ Å, and $c=2.960$ Å (table 5) by heating CrO_2 in water at 450°C under a total pressure of 40,000 lb/in² Christensen (1966), using their material, determined the crystal structure. Table 5 gives the cell constants for guyanaite from Guyana

and Finland and, for comparison, the constants for the synthetic compounds CrOOH (Tombs and others, 1964; Christensen, 1966), ScOOH (Christensen, 1971), and InOOH (Christensen and others, 1964). Until Chenavas and others (1973), reported synthesis of isostructural Fe, Ni, V, and Rh oxyhydroxides, these three were the only substances known to be isostructural with guyanaite (table 24).

Guyanaite is named for Guyana, the country in which the mineral was first found.

Guyanaite, whose identification rests primarily on X-ray powder and chemical data, eskolaite, and perhaps bracewellite are the major components of

merumite. In thin sections of merumite, the vivid green eskolaite contrasts with the brown and red (but sometimes green) guyanaite and the darker brown bracewellite, but it is hardly possible to isolate such intergrown minerals. However, in tiny vugs, prismatic brown pleochroic crystals of guyanaite as much as 0.1 mm long can be isolated (pl. 2, fig. 4). By inspection of a large number of merumite grains, some specimens can be found which have a definitely yellow-brown streak and a sensibly uniform texture and which, by their powder patterns, are almost wholly a massive single-phase guyanaite (pl. 2, fig. 3).

TABLE 5.—Cell constants of guyanaite (from Guyana and Finland), and of CrOOH, ScOOH, and InOOH

Crystal	a (Å)	b (Å)	c (Å)	Space group	Density (calculated in g cm ⁻³)	Reference
Guyanaite (Guyana) —	4.857	4.295	2.958	<i>Pnmm</i>	4.57	This report.
Do —————	4.862	4.314	2.951	--	--	Vuorelainen and others (1968) computed from Berry and Thompson's (1962) X-ray powder data for "Merumite" = guyanaite.
Guyanaite (Finland) --	(2X)4.864	(2X)4.305	(2X)2.959	--	4.81	Vuorelainen and others, 1968.
CrOOH —————	4.861	4.292	2.960	<i>Pnmm</i>	4.57	Tombs and others, 1964; Christensen, 1966.
ScOOH —————	5.150	4.600	3.197	<i>P₂nm</i>		Christensen, 1971.
InOOH —————	4.26±0.01	4.56±0.01	3.27±0.01	<i>Pnmm</i>		Christensen and others, 1964.

Besides the dark-reddish-brown guyanaite, a light-green to greenish-black variety is occasionally found. This variety forms prismatic microcrystalline aggregates, and such a specimen was described under the name of merumite by Berry and Thompson (1962). The compound synthesized by Tombs and others (1964) is described as olive green and light-yellowish-green in transmitted light, with $n \approx 1.9$. Green powdery rounded aggregates as much as 1.0 or 2.0 mm in size and the black merumite in which the aggregates are found both have a green powder and give good X-ray powder patterns of guyanaite.

Concerning the color variation in guyanaite, Alario Franco and Sing (1972) note that the "color of such materials [guyanaite, grimaldiite, and γ -CrOOH] may be deceptive * * * because it is influenced by the change of particle size and (or) the presence at the surface of chromium in different oxidation states."

H. F. W. Taylor and R. Edge, University of Aberdeen (written commun., 1967), studied a specimen consisting "essentially of guyanaite and eskolaite, with a little quartz, ferromagnetic spinel (mag-

netite?) and an ill-crystalline flaky mineral * * * pyrophyllite." A "pinkish mineral" in cavities associated with quartz was probably grimaldiite-meconnellite. They also studied the specimen's thermal behavior, as noted below.

Vuorelainen and others (1968) reported a hydrated oxide of chromium as a new but unnamed mineral from the Outokumpu mine in Finland; their description leaves no doubt that it is guyanaite. The mineral occurs as aggregates of golden-brown to greenish-brown fibers which syntactically replace smaller crystals (less than 1.0 mm in size) of eskolaite.

CHEMISTRY ANALYSES

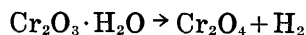
Table 6 gives a microchemical analysis (37 mg) of guyanaite crystals from Guyana and the analysis of guyanaite from Finland by Vuorelainen and others (1968). An analysis of merumite consisting of about two-thirds guyanaite and one-third eskolaite is given in table 2 (analyses A-C).

Guyanaites from both Guyana and Finland would appear from the respective analyses to have com-

positions closer to $2\text{Cr}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, as proposed by Vuorelainen and others (1968), than to $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$, which is known to be correct on the basis of the single-crystal X-ray data. The reason for this difference may be explained by the behavior of CrOOH (guyanaite) when heated.

Tombs and others (1964) found that on heating their synthetic orthorhombic CrOOH ($\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$) converted to Cr_2O_3 in two stages as follows:

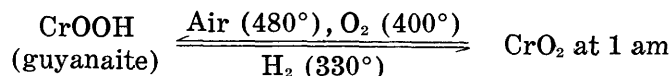
at about 335°C



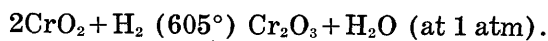
at about $1,000^\circ\text{C}$



and, more recently, Alario Franco and Sing (1972) report the reversible reaction



and the irreversible reaction:



Thus, in a Penfield determination of H_2O^+ in guyanaite, there is a loss of hydrogen initially with formation of CrO_2 instead of simple dehydration with formation of Cr_2O_3 . If this hydrogen is lost, then CrO_2 may remain unreduced to Cr_2O_3 and the H_2O weighed may represent less than the whole H_2O in $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (CrOOH); thus the (erroneous) apparent ratio $2\text{Cr}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ may arise. In the analysis (table 6) only 8.7 percent H_2O was found,

whereas 14.3 percent is required for a formula ROOH .

The determination of loss on ignition should give a correct figure for water, provided that all the Cr_2O_4 is completely converted to Cr_2O_3 on ignition; if not, then the loss on ignition would also be less than the true water content.

If the analysis of merumite from Guyana (table 2, analysis A) is recomputed on such a basis, that is, if the ignition figure 3.5 percent represents the true H_2O content rather than the Penfield determination of 2.3 percent, the composition of the merumite sample (table 2, analysis A) would be:

mineral	constituent	percent
eskolaite	Cr_2O_3	63.5
	CrOOH	28.3
guyanaite	AlOOH	3.6
Total		95.4

If the X-ray fluorescence determination of Cr_2O_3 , 89.2 percent (table 2, analysis B), is used, and the 1.2 percent of spectrographic constituents is added, this, along with 0.1 percent CaO , 3.5 percent H_2O , and 3.1 percent Al_2O_3 , raises the summation of the analysis to 97.1 percent.

THERMAL BEHAVIOR

The findings of Tombs and others (1964) and of Alario Franco and Sing (1972) as to the behavior of orthorhombic CrOOH (guyanaite) on heating were verified experimentally using a merumite

TABLE 6.—Analyses¹ of guyanaite from Guyana and Finland

Constituent	Guyana (microchemical analysis) ²			Finland (mean of seven electron-probe analyses) ³		
	Percent of sample	Equivalent H_2O in $\text{R}_2\text{O}_3 \cdot \text{H}_2\text{O}$	Ratio	Percent of sample	Equivalent H_2O in $\text{R}_2\text{O}_3 \cdot \text{H}_2\text{O}$	Ratio
Cr_2O_3	⁴ 71.7	12.9	0.472	75.76	13.64	0.492
Al_2O_3	⁵ 4.0	.7	.039	1.03	.18	.010
Fe_2O_3	⁶ 4.4	.5	.028	1.47	.16	.009
V_2O_5				6.78	.82	.045
Ti_2O_3	⁷ .86	.1	.006			
Mn_2O_3	⁸ .98	.1	.006			
H_2O^+	⁹ (8.7)					
H_2O^-	⁹ 0					
H_2O (calculated)	14.3			14.96		
Total	96.2	14.3	.551	100.00	14.80	.556
Computed composition,	$(\text{Cr}_{0.89}\text{Al}_{0.04}\text{Fe}_{0.05}\text{Ti}_{0.01}\text{Mn}_{0.01})\text{OOH}$			$(\text{Cr}_{0.88}\text{Al}_{0.202}\text{Fe}_{0.015}\text{V}_{0.080})\text{OOH}$		
	or			or		
	$(\text{Cr}_{1.78}\text{Al}_{0.08}\text{Fe}_{0.10}\text{Ti}_{0.02}\text{O}_3 \cdot \text{H}_2\text{O}$			$\text{Mn}_{0.02}) (\text{Cr}_{1.77}\text{Al}_{0.04}\text{Fe}_{0.03}\text{V}_{0.16})_2\text{O}_3 \cdot \text{H}_2\text{O}$		

¹ Spectrographic analysis of another (massive) sample containing eskolaite gave as minor constituents As_2O_3 , 0.26 percent; V_2O_5 , 0.22 percent; Sb_2O_3 , 0.24 percent; CaO , 0.14 percent; and Au , Cu , Mo , Nb , Pb , and Mg , all 0.0x percent.

² Analyst, Blanche Ingram, U.S. Geological Survey. Approximately 25 mg of sample was fused with a mixture of K_2CO_3 and KClO_4 . The melt was leached with H_2O which separated Fe , Ti , and Mn which remained in the residue, from Cr and Al which went into solution. Tests showed this separation reliable for the amount of Al present. Cr was determined on an aliquot of the water solution by titration with standard ferrous ammonium sulfate.

³ Vuorelainen and others (1968)

⁴ Attempt to determine the oxidation state of chromium chemically failed. The sample was very difficult to get into solution. It was not possible to determine the amount of oxidant that reacted with the sample.

⁵ Aluminum was determined colorimetrically by use of alizarin red S after chromium was volatilized as chromyl chloride.

⁶ The residue from the water leach of the fusion melt was dissolved in HClO_4 , and the iron was determined colorimetrically on an aliquot using 1, 10-phenanthroline.

⁷ Titanium was determined colorimetrically on an aliquot of the residue solution using the Tiron procedure.

⁸ The manganese in an aliquot of the residue solution was oxidized to permanganate and the color measured.

⁹ A 12 mg sample was dried at 110°C . There was no measurable loss at 110°C . The sample was then used to determine water by the Penfield method.

sample consisting largely of guyanaite (X-ray film 00188). When heated to 335°C, the sample gave the powder pattern of CrO₂ formed by heating CrOOH (Thamer and others, 1957) (table 7). On heating to 1,020°C, a pattern closely resembling that of the Finnish eskolaite was obtained (table 8). H. F. W. Taylor and R. Edge (written commun., 1967) confirmed that guyanaite (in merumite) ground to 300 mesh and heated in air to 335°C changes at least partially to CrO₂. They suggest that the change involves migration of protons and electrons to the surface, as in the formation of oxyamphiboles, with no major structural change when guyanaite changes to CrO₂.

Alario Franco and Sing (1972) discuss these reactions in further detail. They note the close structural similarity of the orthorhombic unit cell of CrOOH (guyanaite structure) and the tetragonal unit cell of CrO₂ (rutile type) and observe that, "The introduction of H atoms into the rutile CrO₂ structure allows the formation of hydrogen bonds between the CrO₆ octahedra in one plane, i.e. between central octahedra and corner octahedra, but the overall crystalline structure is only slightly deformed as indicated by the values of the unit-cell parameters. On the other hand, the rhombohedral corundum structure of α -Cr₂O₃ is much more compact ($G=5.21$ g cm⁻³ vs. 4.0 g cm⁻³ for CrO₂) so that hydrogen atoms are not able to force an entry into the lattice and therefore Cr₂O₃ cannot be converted into CrOOH."

X-RAY POWDER DATA

Table 9 gives X-ray powder data of the natural brown guyanaite crystals, of the natural greenish-black massive merumite material, of Berry and Thompson's (1962) "merumite", all three substances from Guyana, of guyanaite from Finland (Vuorelainen and others, 1968), and of synthetic CrOOH (Tombs and others, 1964; Christensen, 1966).

Indexed X-ray powder diffraction patterns show guyanaite to be orthorhombic, space group $Pnmm$, $a=4.857$ A, $b=4.295$ A, $c=2.958$ A, $Z=2$, in close agreement with the data of Tombs and others (1964) and of Christensen (1966).

BRACEWELLITE, CrOOH

OCCURRENCE AND IDENTIFICATION

Minute deep-red to black prismatic crystals of bracewellite having terminal faces line microscopic

TABLE 7.—X-ray powder data of (Cr, Al, Fe, Ti, Mn)₂O₃ from guyanaite, and CrO₂ from CrOOH

(Cr, Al, Fe, Ti, Mn) O ₃ (from guyanaite of film 00188 heated to 335°C) (film 00189)		CrO ₂ (ignited CrOOH) ¹ (Thamer and others, 1957)			
<i>I</i> ²	<i>d</i> ²	<i>I</i>	<i>d</i> (calc)	<i>d</i> (obs)	<i>hkl</i>
vw	B 4.074	-----	-----	-----	-----
vwv	B 3.617	-----	-----	-----	-----
vwv	3.469	-----	-----	-----	-----
vvs	3.130	100	3.126	3.114	110
w	B 2.645	-----	-----	-----	-----
s	2.430	60	2.434	2.424	101
mw	2.211	10	2.211	2.207	200
m	2.129	20	2.132	2.128	111
w	1.981	10	1.977	1.976	210
vwv	B 1.805	-----	-----	-----	-----
vw	E 1.6615	-----	-----	-----	-----
vs	1.634	75	1.636	1.634	211
m	1.564	25	1.563	1.562	220
mw	1.454	15	1.458	1.457	002
w	1.398	15	1.398	1.398	310
-----	-----	10	1.321	1.322	112
m	1.316	25	1.315	1.316	301
-----	-----	<5	1.217	1.219	202
vwv	1.173	-----	1.173	-----	212
vwv	1.131	10	1.130	1.130	321
-----	-----	5	1.105	1.104	400
-----	-----	-----	1.072	-----	410
mw	1.066	10	1.066	1.067	222
w	1.045	5	1.042	1.042	330
w	1.008	20	1.009	1.008	312

¹ $a=4.421$ A, $c=2.916$ A.

² vvs, very very strong; vs, very strong; s, strong; m, medium; w, weak; mw, medium weak; vw, very weak; vwv, very very weak; B, bracewellite? line; E, eskolaite? line.

TABLE 8.—X-ray powder data of (Cr, Al, Fe, Ti, Mn)₂O₃

(Cr, Al, Fe, Ti, Mn) ₂ O ₃ synthetic (from guyanaite of film 00188 heated to 1,020°C) (film 00194)		Cr ₂ O ₃ (eskolaite), Finland Kouvo and Vuorelainen, 1958)	
<i>I</i> ¹	<i>d</i>	<i>I</i>	<i>d</i>
s	3.618	96	3.63
vs	2.656	97	2.665
vs	2.473	94	2.479
vwv	2.397	-----	-----
vw	2.2545	5	2.269
w	2.169	50	2.174
w	1.809	60	1.8146
vvs	1.667	100	1.6746
vwv	1.5765	5	1.6139
vw	1.461	30	1.4656
w	1.428	45	1.4331
vw	1.292	12	1.2971
vwv	1.236	5	1.244
vwv	1.209	-----	-----

¹ vvs, very very strong; vs, very strong; s, strong; w, weak; vw, very weak; vwv, very very weak.

fissures and vugs in merumite. The same substance occurs in crystalline masses, admixed with other merumite minerals; some merumite grains may consist largely of bracewellite. Chemical analysis of such a specimen of massive merumite, mainly bracewellite with eskolaite, is given in table 10. Single crystals of bracewellite, from vugs in merumite, were analyzed by electron probe (table 12). Table 13 gives powder data for two merumite specimens—one (X-ray film 16775), the specimen from which

TABLE 9.—X-ray powder data of guyanaite (from Guyana and Finland), "merumite," and synthetic guyanaite (CrOOH)

Guyanaite										Synthetic guyanaite					
Guyana Pure brown crystals ¹			Guyana Greenish-black massive ²		Guyana "Merumite" (no. 238, Berry and Thompson, 1962)		Finland Vuorelainen and others, 1968			Tombs and others, 1964 ³		Christensen, 1966			
<i>I</i> ⁴	<i>d</i> (obs)	<i>d</i> (calc)	<i>hkl</i>	<i>I</i> ⁴	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>	<i>d</i> (obs)	<i>d</i> (calc)	<i>I</i> ⁴	<i>d</i> (obs)	<i>I</i> (calc)	<i>d</i> (calc)	<i>hkl</i>
				vvw	⁵ Q 3.338										
vvs	3.224	3.217	110	vs	3.221	10	3.23	10	3.225	3.224	s	3.214	306	3.217	110
				mw	⁵ E 2.656										
m	2.524	2.52	101			2	2.53	2	2.525	2.528	m—	2.522	85	2.528	101, 200
		2.436	011										172	2.437	011
vs	2.432	2.428	200	s	2.426	8	2.44	8	2.435	2.432	m+	2.429	65	2.430	200
m	2.178	2.177	111	vw	2.174	2	2.18	3	2.180	2.180	m—	2.174	20	2.178	111
		2.147	020								w—	2.145	20	2.146	020
m	2.115	2.114	210	m	2.113	1	2.12	1	2.115	2.117	m—	2.112	14	2.115	210
		1.964	120												
				vw	⁵ Q 1.811										
ms	1.719	1.720	211	w	1.719	6	1.722	4	1.724	1.722	m	1.720	101	1.721	211
s	1.636	1.636	121	mw	1.636	7	1.639	6	1.640	1.639	m+	1.636	117	1.636	121
ms	1.609	1.609	220	m	1.609	2	1.610	2	1.610	1.612	m—	1.608	44	1.609	220
ms	1.516	1.515	310	mw	1.514	2	1.519	1	1.520	1.517	w	1.515	34	1.516	310
		1.475	002			1	1.475	1	1.480	1.480	w	1.478	22	1.480	002
mw	1.420	1.420	301	vw	1.421	3	1.421	3	1.422	1.422	m—	1.421	35	1.421	301
		1.413	221												
mw	1.375	1.373	130	w	1.377	1	1.382	1	1.376	1.376	w	1.373	48	1.372	130
		1.348	311												
vw	1.342	1.344	112			2	1.342	2	1.344	1.345	m—	1.343	40	1.345	112
		1.293	320												
vw	1.289	1.289	031								w—	1.288	15	1.288	031
vw	1.262	1.263	202								w	1.263	15	1.264	202
		1.246	131								w	1.245	1	1.245	131
		1.233	230								w	1.233	1	1.233	230
		1.218	022										10	1.218	022
		1.214	400								w	1.212	5	1.215	400
vw	1.212	1.212	212										1	1.213	212
vw	1.185	1.185	321								w	1.185	20	1.185	321
		1.168	410												
mw	1.138	1.138	231			1	1.141	1	1.141	1.140			21	1.138	231
		1.089	222			2	1.090	2	1.090	1.090			18	1.089	222
m	1.085	1.087	411										17	1.088	411
		1.074	040										5	1.073	040
mw	1.072	1.072	330												
		1.058	312			1	1.058	1	1.058	1.059			16	1.059	312
m	1.056	1.057	420										9	1.057	420

¹ X-ray film 00188; *a* 4.857 Å, *b* 4.295 Å, *c* 2.958 Å, *Z*=2, *d* calc=4.53.

² X-ray film 16821.

³ *a* 4.861 Å, *b* 4.292 Å, *c* 2.960 Å, *Z*=2, *d* calc=4.57.

⁴ vvs, very very strong; vs, very strong; s, strong; ms, medium strong; m, medium; w, weak; mw, medium weak; vw, very weak; vvw, very very weak.

⁵ Q, quartz and E, eskolaite.

the cell constants of bracewellite were computed, is a massive bracewellite having minor guyanaite, and the other (X-ray film 16761), which was chemically analyzed (table 10; not enough of the first sample was available for analysis) is a merumite having bracewellite, eskolaite, and minor guyanaite. Table 13 also gives powder data for crystals of bracewellite, for goethite (with which bracewellite is isostructural), and for (Guyana) eskolaite. X-ray single-crystal study, as well as a least squares refinement of the powder pattern of massive bracewellite (given in table 13, film 16775) showed orthorhombic symmetry: space group *Pbnm*, with cell constants *a*=4.492±0.003 Å, *b*=9.860±0.005 Å, *c*=2.974±0.002 Å, *Z*=4.

Bracewellite is isostructural with the common minerals diaspore, AlOOH, and goethite, FeOOH

(table 13), as well as with groutite, MnOOH and montroseite, (V,Fe)OOH, and synthetic α-ScOOH, synthetic GaOOH, synthetic CoOOH, and synthetic LaOOH (perhaps with EuOOH and YbOOH also) (table 24). However, no synthesis of bracewellite has been reported.

Bracewellite and guyanaite are superficially much alike, and their powder patterns have a slight resemblance. Bracewellite, however, is a darker reddish brown (almost black) than guyanaite, and the powders of the two minerals are respectively dark brown (almost black) and yellowish brown. Typical crystals of bracewellite are illustrated in plate 4, figure 1.

Bracewellite has been named after Smith Bracewell, formerly director of the British Guiana Geological Survey, who first described merumite.

CHEMISTRY

ANALYSIS

Chemical and spectrographic analyses of a merumite specimen with major bracewellite and minor eskolaite are given in tables 10 and 11.

TABLE 10.—Chemical analysis of merumite containing 70 percent bracewellite and 30 percent eskolaite¹
[Analyst, J. I. Dinnin, U.S. Geological Survey]

Constituent	Percent	Equivalent H ₂ O (assuming R ₂ O ₃ ·H ₂ O)
Cr ₂ O ₃ ²	70.6	8.36
Fe ₂ O ₃ ³	15.1	1.70
Al ₂ O ₃	6.2	1.29
Ti ₂ O ₃	.17	.02
V ₂ O ₃	.64	.08
H ₂ O ⁴	6.9	
Total	99.6	3.09
Ignition loss in argon (at 900°C) ⁴		6.8
Additional loss in oxygen (at 1,000°C)		.6
Total		7.4
Specific gravity 40-mg sample	4.48	±0.045
Specific gravity 20-mg sample	4.45	±0.045
Mean	4.465	±0.045

¹ X-ray powder pattern is given in table 13, (second analysis) film 16761).

² Chromium: A sample was decomposed by digestion with fuming perchloric acid, diluted with water, oxidized with permanganate the excess of which was reduced with hydrochloric acid. Dichromate was reduced with ferrous ammonium sulfate, and titrated with a standard solution of dichromate.

³ Iron: (A) Sample was decomposed by digestion with fuming mixture of sulfuric and phosphoric acids, diluted with water, passed through a silver reductor, and titrated with standardized dichromate. (B) Sample was decomposed by digestion with fuming perchloric acid and treated as above.

⁴ H₂O and ignition loss: A sample in a quartz boat was ignited at 900°C in an argon atmosphere, water being swept through an ignition tube and caught in an Anhydron absorption tube. The weight of the quartz boat before and after ignition represents the ignition loss of the sample. The quartz boat was then ignited at 1,000°C in an oxygen atmosphere. The residue from the ignition was used for the determination of iron. A weighed portion of the ignited sample was digested with fuming perchloric acid, diluted with water and electrolyzed on a mercury cathode to remove chromium and iron. The solution was then diluted to volume, and aliquots used for the following determinations:

Al: Alizarin Red S colorimetric procedure.

Ti: Tiron colorimetric procedure.

V: Phosphotungstomolybdate colorimetric procedure.

TABLE 11.—Spectrographic analysis of merumite containing 70 percent bracewellite and 30 percent eskolaite
[Analyst, H. W. Worthing, U.S. Geological Survey]

Constituent	Percent ¹
Cr, Fe	Major (>10)
Al	3
V	.5
Ti	.3
Si	.1
Co	.03
Mg, Pb, Mn	.02
Cu	.01
Ba, Zr	.005
Ni	.002
Mo	.001
Be, Sr	.0007
Sc, Y, Yb	.0005
Ag	.00002
Looked for but not detected.	K, P, As, Au, B, Bi, Cd, Ce, Ga, Ge, Hf, Hg, In, La, Li, Nb, Pd, Pt, Sb, Sn, Ta, Th, Tl, U, W, Zn.

¹ See footnote on reliability of determinations, table 2, footnote 4.

There is an indication, as seen in table 13 (where the strongest line of guyanite, G, appears as weak in the X-ray pattern) that a small amount of guyanite may be present with major bracewellite and eskolaite. It has been disregarded in the following computations.

The analyses in table 10 can be used in two ways, both of which are unlikely extremes, to compute the composition (and density) of the bracewellite (and eskolaite); the values representing the true compositions are somewhere in between the computer values. The first method would be to assume that all of the H₂O is combined with Cr₂O₃, giving Cr₂O₃·H₂O and (Cr,Fe,Al,Ti,V)₂O₃. The second method would be to assume that all of the H₂O is combined with all of the minor oxides, plus some Cr₂O₃; this gives (Cr,Fe,Al,Ti,V)₂O₃·H₂O + Cr₂O₃. The two computations follow:

	Case 1					
	Per- cent	Mole ratio	Mole ratio	Per- cent	Mole ratio	Per- cent
Cr ₂ O ₃	70.6	464	411	(62.5)	53	(8.1)
Fe ₂ O ₃	15.1	95			95	(15.1)
Al ₂ O ₃	6.2	61			61	(6.2)
Ti ₂ O ₃	.17	1			1	(.17)
V ₂ O ₃	.64	5			5	(.64)
H ₂ O	7.4	411	411	(7.4)		
Total	100.1			(69.9)		(30.2)
	69.9	Cr ₂ O ₃ ·H ₂ O				
	30.2	(Cr _{0.25} Fe _{0.44} Al _{0.29} Ti _{0.00} V _{0.02}) ₂ O ₃				
	100.1					

	Case 2					
	Per- cent	Mole ratio	Mole ratio	Per- cent	Mole ratio	Per- cent
Cr ₂ O ₃	70.6	464	249	(37.9)	215	(32.7)
Fe ₂ O ₃	15.1	95	95	(15.1)		
Al ₂ O ₃	6.2	61	61	(6.2)		
Ti ₂ O ₃	.17	1	1	(.17)		
V ₂ O ₃	.64	5	5	(.64)		
H ₂ O	7.4	411	411	(7.4)		
Total	100.1			(67.4)		(32.7)
	67.4	(Cr _{0.61} Fe _{0.23} Al _{0.15} Ti _{0.00} V _{0.01}) ₂ O ₃ ·H ₂ O				
	32.7	Cr ₂ O ₃				
	100.1					

In the computation of analysis to give density for case 1, where the analyzed sample is computed as 69.9 percent Cr₂O₃·H₂O plus 30.2 percent (Cr_{0.25}Fe_{0.44}Al_{0.29}Ti_{0.00}V_{0.02})₂O₃, we have

$$69.9 \quad + \quad 30.2 \quad = \quad 100.1$$

$$G_{\text{CrOOH}} \quad G_{(\text{Cr}_{0.25}\text{Fe}_{0.44}\text{Al}_{0.29}\text{Ti}_{0.00}\text{V}_{0.02})_2\text{O}_3} \quad 4.465$$

and the computed density of the eskolaite in this sample is 4.86 gcm⁻³. The G_{CrOOH} computes to 4.31 gcm⁻³. These values give a computed density of 4.480 gcm⁻³ for the analyzed sample as compared with a measured 4.465 ± 0.045.

For case 2, where the analyzed sample is computed as 67.4 percent (Cr_{0.61}Fe_{0.23}Al_{0.15}Ti_{0.00}V_{0.01})₂O₃·H₂O plus 32.7 Cr₂O₃, we have

$$\frac{67.4}{G_{(\text{Cr}_{0.61}\text{Fe}_{0.23}\text{Al}_{0.15}\text{Ti}_{0.00}\text{V}_{0.01})_2\text{O}_3 \cdot \text{H}_2\text{O}}} + \frac{32.7}{5.21} = \frac{100.0}{4.465}$$

and the computed density of the bracewellite in this sample is 4.18 gcm^{-3} . These values give a computed density of 4.52 gcm^{-3} for the analyzed sample as compared with a measured 4.465 ± 0.045 .

These two sets of values may be averaged thus:

Eskolaite	
Compositon	Density gcm^{-3}
$(\text{Cr}_{0.25}\text{Fe}_{0.41}\text{Al}_{0.29}\text{Ti}_{0.00}\text{V}_{0.02})_2\text{O}_3$	4.86
Cr_2O_3	5.21
$(\text{Cr}_{0.625}\text{Fe}_{0.22}\text{Al}_{0.145}\text{Ti}_{0.00}\text{V}_{0.01})_2\text{O}_3$	5.035 ± 0.175
Bracewellite	
Compositon	Density gcm^{-3}
CrOOH	4.31 (case 1)
$(\text{Cr}_{0.61}\text{Fe}_{0.23}\text{Al}_{0.15}\text{Ti}_{0.00}\text{V}_{0.01})_2\text{O}_3 \cdot \text{H}_2\text{O}$	4.18 (case 2)
$(\text{Cr}_{0.805}\text{Fe}_{0.115}\text{Al}_{0.075}\text{Ti}_{0.00}\text{V}_{0.005})_2\text{O}_3 \cdot \text{H}_2\text{O}$	4.24 ± 0.065

Finally, these averaged values give computed densities of 4.48 gcm^{-3} (case 1) and 4.50 gcm^{-3} (case 2) for the analyzed sample as compared with the measured 4.465 ± 0.045 , an agreement which indicates the acceptability of the computed values.

An alternative method of computing the density of the bracewellite in this sample is to use the unit cell constants.

$$\text{Thus } G = \frac{\text{mass of unit cell}}{\text{volume of unit cell}},$$

and as for case 1

$$G_{\text{CrOOH}} = \frac{4 \times 85.01}{6.02 \times 10^{23} \times 131.72 \times 10^{-24}} = 4.29 \text{ gcm}^{-3},$$

and as $G_{(\text{Cr}_{0.25}\text{Fe}_{0.44}\text{Al}_{0.29}\text{Ti}_{0.00}\text{V}_{0.02})_2\text{O}_3}$ has been computed to 4.86 gcm^{-3} the computed density of the analyzed sample is 4.46 gcm^{-3} as compared with the measured 4.465 ± 0.045 .

$$\text{For case 2 } G_{(\text{Cr}_{0.61}\text{Fe}_{0.23}\text{Al}_{0.15}\text{Ti}_{0.00}\text{V}_{0.01})_2\text{O}_3 \cdot \text{H}_2\text{O}} = \frac{4 \times 82.1}{6.02 \times 10^{23} \times 131.72 \times 10^{-24}} = 4.14,$$

and as

$$G_{\text{Cr}_2\text{O}_3} = 5.21.$$

the computed density of the analysed sample is 4.49 gcm^{-3} as compared to measured 4.465 ± 0.045

Then,

	From published data	From analysis	From X-ray
$(\text{Cr}_{0.25}\text{Fe}_{0.41}\text{Al}_{0.29}\text{Ti}_{0.00}\text{V}_{0.02})_2\text{O}_3$ (eskolaite)	---	4.86	---
Cr_2O_3	5.21	---	---
$(\text{Cr}_{0.61}\text{Fe}_{0.23}\text{Al}_{0.15}\text{Ti}_{0.00}\text{V}_{0.01})_2\text{O}_3 \cdot \text{H}_2\text{O}$	---	4.18	4.14 (case 2)
CrOOH (bracewellite structure)	---	4.31	4.29 (case 1)
$(\text{Cr}_{0.805}\text{Fe}_{0.115}\text{Al}_{0.075}\text{Ti}_{0.00}\text{V}_{0.005})_2\text{O}_3 \cdot \text{H}_2\text{O}$	---	---	---
(Probable bracewellite composition in analysed sample)	---	Mean 4.245	Mean 4.215

Since both mean values are equally acceptable, their average, 4.23 may be taken as the specific gravity of the bracewellite in the analysed sample, and 4.16 as the specific gravity of bracewellite-structure CrOOH .

ELECTRON PROBE STUDY

Results of an electron probe study of seven crystals of bracewellite and two fragments of merumite are given in table 12. Seven elongate crystals (60–200 μ long) were mounted in epoxy resin and polished; the crystals were prepared in this manner to minimize effects of geometry on X-ray intensities. Two larger fragments of merumite (0.5 mm), from which the individual bracewellite crystals were picked, were similarly prepared for analysis.

Twelve different crystals of bracewellite were dispersed on the surface of a polished beryllium block and were scanned qualitatively for Fe, Al, and Cr. Seven of the 12 crystals showed Fe present as a major constituent, Al significantly above background, and Cr, of course, a major constituent. In 6 of the 7 crystals, raw intensities for Cr decreased in the presence of significant Fe.

Although the results are obviously imprecise, they do indicate that bracewellite varies rather widely in iron content (1–12 percent Fe_2O_3) and, to a lesser degree, in alumina (2–5 percent Al_2O_3).

TABLE 12.—Electron-probe analysis (in percent) of seven crystals of bracewellite and two merumite fragments

["Spec" pure Cr_2O_3 , analyzed FeS_2 , and Al_2O_3 were used as reference standards. CrK_α and FeK_α were measured using the LiF analyzing crystal; AlK_α was measured using potassium acid phthalate. All analyses were performed at 20 kv with a specimen current of 0.01 μamp . Analyst, E. J. Dwornik, U.S. Geological Survey]

Crystal	Al_2O_3	Fe_2O_3	Cr_2O_3	Equivalent H_2O	Sum
Bracewellite					
A	5	12	64	8.7	89.7
B	2	<1	94	10.3	106.3
C	3	<1	95	10.5	108.5
D	5	<1	100	11.35	116.3
E	4	<1	91	10.25	105.2
F	5	12	64	8.73	89.7
G	3	1	95	10.61	109.6
Merumite					
A	3	<1	98	10.84	111.8
B	2	<1	94	10.26	106.3

X-RAY POWDER DATA

In table 13, X-ray powder data for three samples of bracewellite are compared with those for isostructural goethite and eskolaite. It is evident from the X-ray data in the second column that the specimen analyzed in tables 10 and 11 contained, along with bracewellite, considerable eskolaite and very minor guyanite.

TABLE 13.—X-ray powder data for bracewellite, goethite, and eskolaite

I ²	Bracewellite (massive) (X-ray film 16775)		hkl	Merumite (massive bracewellite + eskolaite) ¹ (X-ray film 16761)		Bracewellite (red pure crystals) (X-ray film 16763)		Goethite (Brown, 1961)		Eskolaite (Guyana) (X-ray film 16765)		
	d (obs)	d (calc)		I ²	d (obs)	I ²	d (obs)	I	d (obs)	hkl	I ²	d (obs)
mw	4.92	4.930	020			vw	4.901	10	4.98	020		
vs	4.084	4.088	110	vvs	4.077	vvs	4.065	100	4.18	110		
				s	² E 3.604	vw	² E 3.604				vs	3.601
vw	3.319	3.320	120					10	3.38	120		
						vw	3.314					
w	² G 3.236			w	² G 3.232							
s	2.655	2.653	130	vvs	2.656	vs	2.648	30	2.69	130	vs	2.652
ms	2.547	2.546	021	vw	2.546	vw	2.546	8	2.58	021		
								4	2.520	101		
mw	2.467	2.465	040	s	2.471	w	2.458	16	2.490	040		
ms	2.402	2.405	111	w	2.398	vs	2.404	25	2.452	111	s	2.468
mw	2.216	2.215	121			vw	2.209	10	2.252	121		
ms	2.159	2.161	140	wb	2.168	w	2.149	20	2.192	140	w	2.168
		2.044	220									
		1.979	131					2	2.009	131		
								6	1.920	041		
		1.806	150	w	1.809						w	1.807
w	1.763	1.763	211					8	1.799	211		
vw	1.722	1.748	141					2	1.770	141		
w	1.685	1.684	221			wb	1.678	20	1.721	221		
mw	1.666	1.666	240	sb	1.672			10	1.694	240	s	1.666
w	1.641	1.643	060					4	1.661	060		
vw	1.574	1.574	231					6	1.606	231		
w	1.542	1.543	160			vw	1.5395	16	1.546	151, 160		
vw	1.484	1.482	250			vw	1.485	10	1.509	250, 002		
								4	1.467	320		
w	1.461	1.450	241								vw	1.460
								10	1.453	061		
wb	1.428	1.424	022	w	1.430						w	1.426
						vw	1.417	2	1.418	112		
								8	1.392	330		
								8	1.357	331		
vw	1.341	1.344	170									
m	1.293	1.297	132	vw	1.298			8	1.317	321	vw	1.30
								2	1.264	331		
								2	1.241	142		
								2	1.198	341		

¹ See table 10 for analysis.² vvs, very very strong; vs, very strong; s, strong; ms, medium strong; m, medium; w, weak; mw, medium weak; vw, very weak; vvw, very very weak; b, broad; E, strongest line of eskolaite; G, strongest line of guyanaite.

GRIMALDIITE CrOOH and MCCONNELLITE CrOOCu

OCCURRENCE

Well developed tabular deep-red rhombohedral crystals as much as 1 mm in size and having perfect cleavage, found in vugs in the merumite, proved to be inseparable intergrowths (polycrystals) of two isostructural phases, CrOOH and CrOOCu, both rhombohedral. Their identification has been possible because of the close correspondence of their chemical and X-ray data with those of the synthetic substances. These phases have been named grimaldiite and mcconnellite, respectively, for Dr. F. S. Grimaldi of the U. S. Geological Survey and for Dr. R. B. McConnell, former Director of the British Guiana Geological Survey.

A typical mode of occurrence is illustrated in plate 1, figure 4, a sawed face of merumite, and in plate 3, figure 1. Small granular aggregates of pink

grimaldiite-mcconnellite fill vugs (frontispiece, lower left). The aggregates themselves consist of more or less euhedral single crystals such as those shown in plate 5, figure 1.

Only very rarely has pure natural rhombohedral CrOOH been observed as clear deep-red fragments of microscopic crystals broken in the crushing of specimens of merumite for study; these fragments have been sufficient for single-crystal X-ray study but not for chemical analysis. Almost all known grimaldiite occurs as well-developed tabular rhombohedral crystals which are intergrowths of grimaldiite and the isostructural mcconnellite. These composite crystals are characteristically turbid, translucent rather than clear, and vary as to X-ray powder pattern and optical character according to the relative amounts of the two substances forming the aggregate. Chemical analyses have also, necessarily, been made on such composite crystals. Nevertheless, the two minerals can be clearly resolved

with the electron probe, and their distribution in the crystals has been individually photographed by X-ray fluorescence (pl. 4, fig. 2).

PHYSICAL PROPERTIES

The physical properties—refractive indices and density—vary from one polycrystal to another, as is shown by the natural crystals. As the electron-probe photographs indicate, consistent optical measurements cannot be obtained.

The available optical data for (synthetic) hexagonal CrOOH are $\epsilon=1.975$, $\omega=2.155$ (measured in sodium light), giving a geometric mean of 2.093; the mean refractive index from specific refractive energies is 2.1 (Douglass, 1957). Earlier, a measured refractive index of approximately 2.0 ± 0.1 was given by Shafer and Roy (1954). For the density Douglass (1957) reported $4.11 \pm 0.03 \text{ gm}^{-3}$ as a measured value and calculated 4.10 from X-ray data; even earlier, Laubengayer and McCune (1952) reported 4.12 gm^{-3} (measured value). No optical data were reported for CrOOH (mcconnellite), but $\frac{1}{3}(2\omega + \epsilon)$ can be calculated as 2.29 by the Gladstone-Dale formula, using the measured density 5.49 gm^{-3} (calculated, 5.609 gm^{-3}) of Dannhauser and Vaughan (1955). Stroupe (1949) gave a "rough" density of 7.0 gm^{-3} .

Accordingly, for the natural complex grimaldiite-mcconnellite crystals, observed refractive indices should range from ϵ of CrOOH (1.975) to the ω of CrOOCu (somewhat higher than 2.29), taking into account slight changes which reflect the Al and Fe

in the two compounds. However, because of the very irregular distribution of the two compounds in the crystal, it is unlikely that any precise determinations are feasible.

CHEMISTRY

A chemical analysis of a large number of crystals of the grimaldiite-mcconnellite intergrowth and supplementary microspectrographic data are given in tables 14 and 15. An X-ray pattern (table 16) can be interpreted from our knowledge of the X-ray crystallography of the synthetic phases; the only ambiguities are the roles of Al_2O_3 and Fe_2O_3 as substitutions for Cr_2O_3 in the two compounds. Depending on this, the crystal aggregates in the analyzed sample consist of about 80.5–86.5 percent grimaldiite, the remainder being mostly mcconnellite.

The loss on ignition is presumably low by 0.55 percent because of oxidation of Cu_2O , and the analysis is adjusted accordingly. Tombs and others (1964) found that rhombohedral CrOOH, unlike the orthorhombic form (which is guyanaite), decomposed only partially at 350°C to a mixture of CrO_2 and Cr_2O_3 . The ignition loss, however, should represent all of the water in the grimaldiite (mcconnellite being assumed to have no hydrogen substituting for copper).

The chemical data are consistent with the average relative proportions of CrOOH and CrOOCu shown by electron probe (pl. 4, fig. 2).

TABLE 14.—Chemical analysis¹ of grimaldiite-mcconnellite polycrystals
[Analysts, Frank Cuttitta and H. J. Rose, Jr., U.S. Geological Survey]

	Wt. percent	Wt. percent recomputed	Mole ratio	(Al, Fe) $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$		$\text{Cr}_2\text{O}_3 \cdot \text{Cu}_2\text{O}$		$\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$		H_2O	
				Mole ratio	Percent	Mole ratio	Percent	Mole ratio	Percent	Mole ratio	Percent
Cr_2O_3 -----	77.3	77.3	509	-----	-----	35	5.3	474	72.0	-----	-----
CuO -----	5.5	(Cu_2O) 4.95	35	-----	-----	35	4.95	-----	-----	-----	-----
Al_2O_3 -----	4.3	4.3	42	42	4.3	-----	-----	-----	-----	-----	-----
Fe_2O_3 -----	.85	.85	5	5	.85	-----	-----	-----	-----	-----	-----
SiO -----	.42	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
H_2O -----	.00	.00	-----	-----	-----	-----	-----	-----	-----	-----	-----
Ignition loss -----	11.5	(H_2O^+) 12.05	669	47	.85	-----	-----	474	8.5	148	2.7
Total percent	99.87	99.45	-----	-----	6.00	-----	10.25	-----	80.5	-----	2.7
Total mole ratio	-----	-----	1,260	94	-----	70	-----	948	-----	148	-----

¹ Microanalysis (total sample 9.35 mg).

The analytical methods used for the microdeterminations were: Cr and Cu by X-ray fluorescence; Si, Al and Fe by spectrophotometry, using heteropolymolybdenum blue, alizarin S, and 1, 10-phenanthroline, respectively, as chromogenic agent; and H_2O^- and loss on ignition by gravimetry.

Copper is recomputed as Cu_2O , rather than the CuO reported by the analyst. On ignition, the Cu_2O would presumably oxidize to CuO, affecting the ignition loss negatively by gain of 0.6 percent of oxygen. The thermal decomposition of rhombohedral CrOOH is discussed in some detail by Tombs and others (1964); its behavior is quite different from that of orthorhombic CrOOH. Whereas the latter readily and completely converts to stable CrO_2 at 350°C , rhombohedral CrOOH at this temperature changes slowly and partially to a mixture of CrO , and Cr_2O_3 ; when the rhombohedral CrOOH is completely changed, there is no reduction of CrO_2 to Cr_2O_3 .

The recomputed ignition loss 12.05 percent, is obtained by adding to 11.5 percent the oxygen gain (0.55 percent) of $\text{Cu}_2\text{O} + \text{O} \rightarrow 2\text{CuO}$.

Both analysis and X-ray pattern (table 16) indicate the presence of quartz (less than 0.5 percent). Because the analyzed material was obtained from a merumite-quartz aggregate, this is not surprising.

Interpretation of analysis

Constituent	Percent
Grimaldiite (Cr, Al, Fe)OOH -----	80.5 -86.5
Mcconnellite (Cr, Al, Fe)OOCu -----	16.25-10.25
H_2O (excess) -----	2.7 - 2.7
Total -----	99.45-99.45

TABLE 15.—*Microspectrographic analysis of grimaldiite-mcconnellite polycrystals*¹
[Analyst, C. L. Waring, U.S. Geological Survey]

Constituent	Percent ²
Cr -----	>10
Cu -----	10
Al -----	3
Fe, Zn ³ -----	.3
Ti -----	.03
Mg, Ca, Si -----	.01

¹ Sample (1 mg) is different from that in table 12.

² See footnote on reliability of determinations, table 2, footnote 4.

³ The Zn may represent chromian gahnite.

ELECTRON-PROBE ANALYSIS

Electron-probe analysis of the polycrystals (pl. 4, fig. 2) showed a high chromium content throughout the intergrowth. Parallel to the cleavage, layers having a relatively high copper content alternate with copper-free layers (within the limits of detection). X-ray powder diffraction (table 16) and single-crystal (table 17) studies showed that these polycrystals are composed of both CrOOH (grimaldiite) and CrOOCu (mcconnellite).

Electron-beam scanning images of the two new interlayered mineral phases were prepared to show distribution of copper and chromium within several grains. The individual "books" were prepared by imbedding the grains in epoxy, orienting them so that the electron beam would be scanning at a slight angle to the basal cleavage plane, or, essentially, so that the beam would be "looking at the edge." Several grains show alternating Cu-Cr and Cr layers. On other grains, copper was detectable only on the outer edges of the layers on which it appeared.

H. T. Evans, Jr. (oral commun., 1966) noted that in the isostructural grimaldiite and mcconnellite, the CrO₂ complex forms layers which are then connected by the cations—in this case H⁺ and Cu⁺. Interlayer substitution in this respect should take place easily, but the large difference in atomic diameters of H⁺ and Cu⁺ interferes. Alternation of layers at the atomic level is possible, however. It may also be noted that the *a* parameters are almost identical and that the *c* parameters vary according to the diameter of the cation.

Plate 4, fig. 2, shows electron-beam scans of the composite grimaldiite-mcconnellite crystals; the distribution of the mcconnellite in a well-defined second phase, not in random distribution, is clearly shown by the fluorescence of the copper.

X-RAY DATA

Single-crystal study of isolated crystals of pure grimaldiite (these are very rare; almost all gri-

maldiite is intergrown with mcconnellite) showed that it is rhombohedral, space group $R\bar{3}m$, with unit cell (in hexagonal setting) $a=2.986\pm 0.009$ A, $c=13.40\pm 0.04$ A, in rhombohedral setting $a=4.787\pm 0.005$ A, $\alpha_{rh}=36.3\pm 0.1^\circ$, $Z=1$. Douglass (1957) reported $a=2.984\pm 0.003$ A, $c=13.40\pm 0.01$ A for synthetic rhombohedral CrOOH prepared by thermal decomposition of aqueous chromic acid. The strongest X-ray lines of grimaldiite (table 16) are in good agreement with the data of Thamer and others (1957) for the synthetic compound. The strongest X-ray diffraction lines of mcconnellite (table 16), from a pattern of a mixed crystals of mcconnellite and grimaldiite, agree closely with the data of Stroupe (1949) for synthetic CrOOCu prepared by thermal decomposition of precipitated copper ammonium chromate.

Unit-cell dimensions from least squares refinement of indexed X-ray powder-diffraction data for mcconnellite are in good agreement with those obtained by Dannhauser and Vaughan (1955), who showed that CrOOCu is rhombohedral and determined the crystal structure. The crystal structures determined by Douglass (1957) and by Dannhauser and Vaughan (1955) show that grimaldiite and mcconnellite are isostructural, so their oriented intergrowth is understandable.

Strunz (1970, p. 175) groups mcconnellite and delafossite with AlOOCu and GaOOCu as oxides and (p. 218) groups grimaldiite and heterogenite as hydroxides.

From the *d*-spacings of film 16794 (table 16), the cell constants of both grimaldiite and mcconnellite were obtained and are given in table 17. With these are shown the similar cell constants for other isotypic minerals and synthetic compounds.

PREVIOUS SYNTHESSES OF RHOMBOHEDRAL CrOOH AND CrOOCu

Laubengayer and McCune (1952) prepared rhombohedral CrOOH hydrothermally at 145°C, and Shafer and Roy (1954) cite Simon and others (1930) as having first prepared crystalline chromium oxyhydroxide hydrothermally at 200°C and 15 atm. Shafer and Roy (1954) prepared crystalline CrOOH from a gel at 230°C and 4 atm for 322 hr. Thamer and others (1957) synthesized rhombohedral CrOOH by heating aqueous chromic acid in sulfuric acid solutions to 300°–325°C; they gave comprehensive data on its morphology, physical properties, and X-ray powder pattern (table 16). Douglass (1957) determined the structure of rhombohedral CrOOH, and L. H. Jones (in Douglass,

TABLE 17.—Cell constants of grimaldiite, mcconnellite, and related substances
[Ditrigonal-scalenohedral $R\bar{3}m$]

	a (angstroms)	c (angstroms)	Reference
Grimaldiite	2.973 ±0.002A	13.392 ±0.01A	This report.
CrOOH	2.984 ±0.003	13.40 ±0.01	Douglass, 1957.
Heterogenite (stainierite) CoOOH.	2.855	13.156	Kondrashev and Federova, 1954.
Mcconnellite	2.983 ±0.004	17.160 ±0.031	This report.
CrOOCu	2.9747±0.0014	17.1015±0.0005	Dannhauser and Vaughan, 1955.
FeOOAg	3.041	18.55	Croft, Tombs, and England, 1964.
Delafossite FeOOCu.	3.038	17.00	Pabst, 1938.
AlOOCu	2.85	16.9	Hahn and de Lorent, 1955.
GaOOCu	3.03	17.1	Do.
CoOPt	2.8300±0.0004	17.837 ±0.002	Shannon, Rogers, and Prewitt, 1969.
CoOPd	2.8300±0.0003	17.743 ±0.002	Do.
CrOOPd	2.9230±0.0003	18.087 ±0.003	Do.
RhOOPd	3.0209±0.0002	18.083 ±0.002	Do.
CoOOCu	2.8488±0.0001	16.920 ±0.002	Do.
RhOOCu	3.074 ±0.001	17.094 ±0.009	Do.
CoOOAg	2.8729±0.0002	18.336 ±0.002	Do.
CrOOAg	2.9843±0.0004	18.511 ±0.004	Do.
RhOOAg	3.0684±0.0004	18.579 ±0.004	Do.
GaOOAg	2.9889±0.0002	18.534 ±0.002	Do.
InOOAg	3.2772±0.0003	18.881 ±0.003	Do.
ScOOAg	3.2112±0.0002	18.538 ±0.002	Do.
TlOOAg	3.568 ±0.002	18.818 ±0.006	Do.
AlOOAg	2.890 ±0.002	18.27 ±0.02	Gessner, W., 1967.
Feitknechtite MnOOH.		13.18	R. C. Erd, written commun., 1972.
	3.1?		XPDF-18 804.

questioned by the work of Buist and others (1966), who found in an experimental study of the system Cu-Fe-O no phase FeOOCu (delafossite), only one of composition given as $3\text{Cu}_2\text{O}\cdot\text{Fe}_3\text{O}_4$. Moreover, with the X-ray diffraction patterns of natural delafossite from three localities, they give that of their $3\text{Cu}_2\text{O}\cdot\text{Fe}_3\text{O}_4$; the patterns are closely similar.

However, the existence of $3\text{Cu}_2\text{O}\cdot\text{Fe}_3\text{O}_4$ was discredited by others. Yund and Kullerud (1964) determined equilibrium assemblages in the system Cu-Fe-O at 800°C and below, finding delafossite CuFeO_2 and copper ferrite CuFe_2O_4 (a spinel) were the only ternary phases. Similarly, Wiedersich and others (1968) showed that from initial mixtures of

Cu_2O or CuO and Fe_2O_3 , or of Cu_2O and FeO or Fe_3O_4 , only CuFeO_2 (delafossite) and sometimes a spinel phase formed; no mixture yielded a compound $\text{Cu}_6\text{Fe}_3\text{O}_7$ ($3\text{Cu}_2\text{O}\cdot\text{Fe}_3\text{O}_4$). Finally, the structural study of Douglass (1957) establishes the composition of mcconnellite (CrOOCu) as valid.

Mcconnellite, CrOOCu , is therefore, as suggested by Dannhauser and Vaughan (1955), isostructural with delafossite, FeOOCu . Hey (1968) has analyzed natural delafossite from Nizhni Tagil, U.S.S.R. (the type locality) and Kimberly, Nevada, confirming the accepted formula FeOOCu . He also observes that natural delafossite is clearly not a high-temperature phase, as it is often closely associated with kaolinite; this may be of interest with reference to the merumite mineralogy, including mcconnellite, with which another hydrous silicate, pyrophyllite, is commonly associated.

Both mcconnellite and grimaldiite are isostructural with CoOOH (heterogenite), MnOOH (feitknechtite), and NiOOH (synthetic), and with NaHF_2 and CsICl_2 (table 24).

γ -CrOOH (SYNTHETIC)

Besides the three new natural polymorphs of CrOOH found in merumite, a fourth is known only as a synthetic product. It is termed γ -CrOOH and is very probably isostructural with the common orthorhombic dipyramidal minerals boehmite (γ - AlOOH), lepidocrocite (γ - FeOOH), and synthetic γ - ScOOH , whose cell constants are all given in table 19. Alario Franco and Sing (1972) refer to " γ -CrOOH" as "similar to boehmite." However, no single-crystal work has been done on γ -CrOOH; Christensen (written commun., 1971) notes that " γ -CrOOH is very difficult to prepare in the laboratory, so it is not so surprising that this form is not found in nature."

SYNTHESIS

Hund (1959) describes γ -CrOOH as green, prepared by heating in an autoclave a solution of sodium chromate with sodium formate or sulfur (as reducing agents) for 10 hr at 250°–270°C. Hund also gives infrared absorption curves for the γ forms of AlOOH , CrOOH , and FeOOH , further showing the isotopy.

By reduction of sodium chromate with hydrogen, at 290°C, 140 atm pressure, for 2 hr, Torokin and others (1968) obtained an emerald-green hydrous oxide having 2.29 moles of H_2O per one mole of Cr_2O_3 . On further heating to 320°C, the water content decreased to 1.54 moles and at 340°–360°C, with

slight loss of water content (to 1.51 moles), there was a color change to dirty violet, interpreted as an inversion from γ -CrOOH to α -CrOOH (grimaldiite). The latter compound was also formed (from chromium nitrate solution and ammonia) at 320°, 200 atm for 2 hr.

X-RAY POWDER DATA AND CELL CONSTANTS

Torokin and others (1968) discuss γ -CrOOH, giving powder data. Their data, with that of lepidocrocite (Rooksby, 1951), are given in table 18. Their d spacings have been computed to give the cell constants of table 19; these have been used to index the pattern.

CHROMIAN GAHNITE

PROPERTIES

Violet octahedral crystals (plate 5, fig. 2) of chromian gahnite, $Zn(Al_{0.7}Cr_{0.3})_2O_4$, are frequently

associated with grimaldiite-mcconnellite polycrystals but are inconspicuous because of their extremely small size (usually less than 0.02 mm) and similarity in color to the grimaldiite-mcconnellite. Optically, they are anisotropic and show marked complex twinning, opposite octants appearing to extinguish together. The index of refraction is about 1.915. The mineral gave excellent X-ray powder patterns. Ball mounts were used because too little material was available for standard spindles. The X-ray data are given in table 20.

Table 15 gives a microspectrographic analysis of grimaldiite-mcconnellite containing 0.3 percent Zn; if this is assumed to be in the chromian gahnite, there would be nearly 1 percent of this mineral present in the sample, somewhat more than is usually observed.

Figure 4 is a graph of unit cell edge plotted against compositions from 100 percent $ZnAl_2O_4$ to 100 percent $ZnCr_2O_4$ using the data of table 20. According to this graph the composition of the Guyana chromian gahnite is $Zn(Al_{0.7}Cr_{0.3})_2O_4$.

TABLE 18.—X-ray powder patterns of γ -CrOOH and lepidocrocite

γ -CrOOH (Torokin and others, 1968)				Lepidocrocite (Rooksby, 1951)		
l	d	d (calc) ¹	hkl	l	d	hkl
40	6.38	6.35	020	100	6.26	020
40	3.30	3.31	120	90	3.29	120
		2.84	011	10 R	2.79	011
90	2.40	2.40	031	80	2.47	031
		2.29	111	20	2.36	111
		2.11	060	20	2.09	131, 060
100	1.962	1.943	200	70	1.937	051, 200
10	1.885	1.916	051			
		1.858	160	20	1.848	220
		1.718	151	40	1.732	151
		1.588	080	20	1.566	080
				20	1.535	002
10	1.512	1.511	231	40	1.524	201
				10 R	1.496	022
		1.470	180	10	1.449	180
		1.432	171	20	1.433	171
60	1.406	1.422	022	10	1.418	260
				10	1.389	122
		1.364	251	30	1.367	251
		1.270	091	10	1.261	091, 320
		1.229	280	10	1.213	280
		1.208	191	20	1.196	022, 191
		1.207	1·10·0	20	1.189	1·10·0
30	1.183	1.199	340			
		1.179	311			
		1.105	360	20 B	1.10	
		1.095	242			
		1.074	082	40	1.075	

¹ Calculated from Torokin and others (1968), X-ray powder data giving approximate cell parameters in table 19.

TABLE 19.—Cell constants (in Å) of γ -CrOOH and related compounds

	a	b	c	Reference
γ -CrOOH ¹	3.89 ±0.02	12.70 ±0.13	2.92 ±0.02	This report
Böhmite (γ -AlOOH)	3.69	12.2	2.86	Reichert and Yost, 1946
Lepidocrocite (γ -FeOOH)	3.88	12.54	3.07	Rooksby, 1951
Do	4.01	13.01	3.24	Milligan and McAtee, 1956
γ -ScOOH	4.015	13.04	3.244	Auer-Welsbach and Seifert, 1962

¹ Computed from powder data of Torokin and others (1968); the values are approximate.

ELECTRON-PROBE ANALYSIS

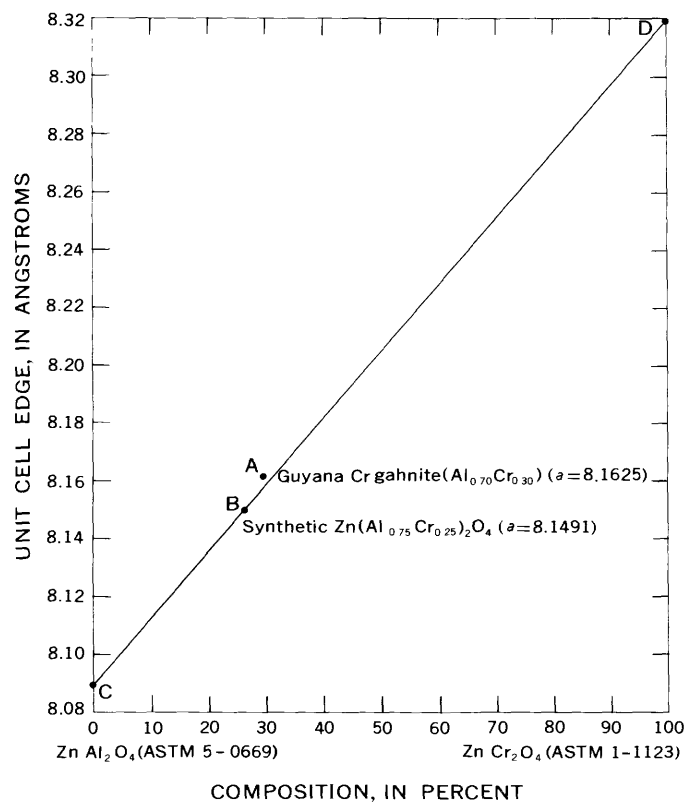


FIGURE 4.—Graph of unit cell edge versus composition in natural and synthetic chromian gahnite. A, Composition of chromian gahnite from Guyana was computed from cubic cell constant. B, Cubic cell constant of synthetic chromian gahnite was computed from X-ray powder pattern. C, Composition and cubic cell constant of $ZnAl_2O_4$. D, Composition and cubic cell constant of $ZnCr_2O_4$.

A procedure for probe analysis was developed by E. J. Dwornik and H. J. Rose, Jr. using willemite and sphalerite as standards for zinc; pure alumina, synthetic $MgAl_2O_4$, and analyzed chromites as standards for aluminum; and analyzed chromite as standard for chromium. Synthesized spinels ranging in composition from $ZnAl_2O_4$ to $ZnCr_2O_4$ could not conveniently be used as reference standard because of extremely fine grain size and inhomogeneity, as exhibited in preliminary electron-probe intensity measurements and variations in luminescence under electron excitation. The probe was operated at 20 kv with a specimen current of 0.05 μ amp.

An average composition (in percent) for 10 crystals, varying in size from 20–40 μ m, is ZnO, 46; Al_2O_3 , 30; and Cr_2O_3 , 25; all ± 10 percent.

The composition computed (in percent) from unit-cell data is ZnO, 41; Al_2O_3 , 36; and Cr_2O_3 , 23.

X-RAY DATA

Table 20 gives X-ray powder data for the chromian gahnite from Guyana and for related spinels.

OTHER CHROMIAN GAHNITES AND ZINCIAN CHROMITES

Chromian spinels are usually black chromites, or colored spinels, having a small chromium content. The Guyana gahnite contains 23.4 percent Cr_2O_3 , by far the highest percentage yet known. John L. Baum (written commun., 1969) reports minute reddish-brown octahedral chromium zinc spinel from the Sterling mine at Ogdensburg, N. J. Clifford Frondel

TABLE 20.—X-ray powder data for chromian gahnite $Zn(Al_{0.7}, Cr_{0.3})_2O_4$ from Guyana and synthetic spinels

$ZnCr_2O_4^1$		$Zn_{0.7}Al_{0.3}Cr_{0.3}O_4^2$		$Zn(Al_{0.75}, Cr_{0.25})_2O_4^3$		$ZnAl_2O_4^4$		
<i>l</i>	<i>d</i>	<i>l</i> ⁵	<i>d</i> (obs)	<i>d</i> (calc)	<i>l</i> ⁵	<i>d</i>	<i>l</i>	<i>hkl</i>
							3	111
48	2.92	vs	2.888	2.886	vs	2.884	84	220
100	2.50	vvs	2.463	2.461	vvs	2.456	100	311
3	2.40						1	222
10	2.07	w	2.040	2.040	w	2.038	8	400
							10	331
							10	331
25	1.69	mw	1.663	1.666	s	1.664	24	422
50	1.60	s	1.570	1.571	vs	1.568	40	511
60	1.47	s	1.442	1.443	vs	1.437	43	440
							1	531
5	1.31	vw	1.291	1.290	w	1.289	6	620
8	1.27	w	1.246	1.245	mw	1.243	9	533
1	1.20						1	622
							<1	444
							1	711
							9	642
7	1.11	vw	1.095	1.091			12	731
12	1.08						4	800
4	1.04						1	733
							5	822
		vw	.965	.962			5	822
		vw	.944	.942			9	751

Plus additional weak lines.

¹ Synthetic zinc chromite, $ZnCr_2O_4$, prepared by New Jersey Zinc Co., XPDF card 1-1122. $a=8.32\text{\AA}$.

² Chromian gahnite, $Zn(Al_{0.7}, Cr_{0.3})_2O_4$, from Guyana. $a=8.1625\text{\AA}$.

³ Synthetic compound, $Zn(Al_{0.75}, Cr_{0.25})_2O_4$, prepared by Jun Ito, Harvard University (written commun., 1968). $a=8.1491\text{\AA}$.

⁴ Synthetic zinc aluminate (gahnite), $ZnAl_2O_4$, prepared by RCA Laboratory, XPDF 5-0669. $a=8.0848\text{\AA}$.

⁵ s, strong; vs, very strong; vvs, very very strong; w, weak; mw, moderately weak; vw, very weak.

(written commun., 1968) reports that microprobe analyses of these crystals showed more aluminum than chromium; they were dark green to brownish black in color.

In the Outokumpu mine, Finland, where eskolaite was found, there is a chromite with 5.8 percent ZnO (Thayer and others, 1964). A chromite from Norway has 2.62 percent ZnO (Donath, 1931) and a chromite from Maryland contains 0.6 percent ZnO (Pearre and Heyl, 1960). Seeliger and Mücke (1969) describe donathite as a tetragonal analog of ferrian chromite that contains up to 2.62 percent ZnO, is opaque, dark brown streak, strongly magnetic, having composition $(\text{Fe}_{0.787}\text{Mg}_{0.137}\text{Zn}_{0.076}) \cdot (\text{Cr}_{0.642}\text{Fe}_{0.350}\text{Al}_{0.008})_2\text{O}_4$.

CHROMIAN PYROPHYLLITE

Pyrophyllite is almost as abundant an accessory mineral in merumite as is quartz, although, because of pyrophyllite's softness, it has never been observed on the naturally worn surface of merumite specimens, whereas quartz occasionally is. However, on breaking open a merumite specimen, radial aggregates of white, bluish-green, or sometimes yellowish-brown pyrophyllite, as much as 1-2 mm across, are often seen.

Two X-ray films, 178 and 305, the latter of the blue-green pyrophyllite, identify the mineral.

The chromium content of two selected greenish flakes was determined by X-ray fluorescence (E. J. Dwornik, analyst) as 2.2 percent and 2.6 percent Cr_2O_3 respectively; therefore, about a tenth of Al_2O_3 is replaced by Cr_2O_3 .

Chromian pyrophyllite has also been reported from Salzburg, Austria (Meixner, 1961), with about 1 percent Cr ($\cong 2.93$ percent Cr_2O_3). Here it is found, associated with quartz and ankeritic carbonates, in a bleached zone around gersdorffite-bearing veins and is derived from hydrothermal alteration of sericite.

GOLD (AND SILVER) IN MERUMITE

Gold is present in merumite as irregularly subrounded grains, a few showing vague octahedral outlines, some as large as 0.05 cm but generally much smaller. The large merumite specimen having abundant grimaldiite-mcconnellite and quartz (plate 1, fig. 4) is especially rich; the gold content is estimated as over 10 oz/ton. The gold is bright yellow, indicating little silver, and shows no evidence of wear or attrition. It is believed to be a primary mine-

ral, formed with the chromium mineralization following that of quartz.

Plate 3, figure 2, shows gold in a polished section of merumite.

Several attempts were made to determine the gold content of selected merumite specimens. The results are given in table 3 and in table 21. In summary, six samples of merumite were analyzed for gold and silver; gold was found in all, although some methods of analysis (spectrographic) did not reveal small amounts; silver accompanies the gold, although in a very small ratio, and did not exceed 1 ppm in samples with less than 4 ppm gold; in two samples gold was as high as 2 oz/ton and 23 oz/ton.

ACCESSORY MINERALS FROM DIRECTOR CREEK

A sample of White Sand Formation, about 0.8 km (0.5 mile) northeast of the Director Creek merumite deposit, contained a rather scanty assemblage of heavy minerals—about 80 percent rutile, 10 percent zircon, also apatite, tourmaline, andalusite, and possibly, hypersthene and chromite. Chromite is a common though rather sparing detrital mineral elsewhere in the region. Hypersthene and andalusite occur characteristically downstream from dolerite intrusions.

The rutile is similar to that found with merumite;

TABLE 21.—Gold and silver in six fragments of merumite

Sample ¹	Au	Ag
A----60 ppm (2 oz/ton) ²	0.03 percent (10 oz/ton) ⁴	3 ppm ³ 0.003 percent ⁴
B----4 ppm ²	Not detected ⁴	<1 ppm ³ Not detected. ⁴
C----2 ppm ²	Not detected ⁴	<1 ppm ³ Not detected. ⁴
D----0.5 ppm ²	Not detected ⁴	<1 ppm ³ Not detected. ⁴
E----Looked for but Not detected ² .	0.7 ppm ⁶ 0.9 ppm ⁷	0.00002 percent ⁵ (0.2 ppm)
F----0.07 percent (23 oz/ton) ⁸		0.0017 percent ⁸ (10 ppm)

¹ Sample:

A Fragments of merumite not themselves showing visible gold but from a specimen (figs. 3 and 4) known to be rich in visible gold. Because sample A was selected by deleting all fragments in which gold was visible, the value of 2 oz/ton is probably much lower than the true value for this specimen.

B, C, D Fragments of merumite in which no visible gold was known.

E Fragments of merumite, consisting of about 30 percent eskolaite and 70 percent bracewellite, in which gold was not known to be present. See tables 10 and 11.

F Fragments of merumite, consisting of about 62 percent eskolaite and 38 percent guyanaite, in which gold was not known to be present. See table 2, analysis C.

²Cyanide-atomic absorption method; 10-gram samples; analyst, J. D. Mensik.

³ HNO_3 boil-atomic absorption method; 1-gram samples; analysts, J. D. Mensik and J. A. Thomas.

⁴Spectrographic method; analyst G. W. Sears, Jr. "Results are reported in percent to the nearest number in the series 1, 0.7, 0.5, 0.3, 0.2, 0.15, and 0.1, etc., which represent approximate mid-points of interval data on a geometric scale. The assigned interval for semiquantitative results will include the quantitative value about 30 percent of the time."

⁵Spectrographic method, as above; analyst, Helen W. Worthing.

⁶Cyanide-lead decomposition; 1-gram sample; analyst, John Marinenko. Gold determined fluorimetrically as the Rhodamine B Chloraurate.

⁷Aqua regia leach decomposition and Te precipitation; 1-gram sample; analyst, John Marinenko.

Gold determined fluorimetrically as the Rhodamine B Chloraurate.

⁸Spectrographic, as above, analyst, Helen W. Worthing.

the zircon occurs in both well-rounded and prismatic pinkish-brown grains, the tourmaline in brown rounded grains, and the andalusite (pleochroic) in pink grains. The chromite(?) is in rounded, also octahedral, grains.

Overlying the merumite in Director Creek is a pinkish to red clayey soil with numerous quartz pebbles. Very little merumite was found in it, but what was found occurred with reddish mottled quartzite, some showing secondary quartz overgrowths, and friable quartz-hydromuscovite grains.

Below the merumite is about 0-3 m of reddish clayey and pebbly sand having much hydromuscovite and some pumiceous fragments; rutile, zircon, and tourmaline were present.

Besides quartz, rutile, zircon, and topaz, the pinkish sand from which the merumite is washed in the batelle contains, in much less quantity, tourmaline, staurolite, and spinel. The rutile is quite variable in color, from lead gray to reddish brown and mottled;

some grains contain anatase. Many of the brown grains show a bipyramidal habit. The zircon, usually altered, is in anhedral grains, and shows anomalously low indices of refraction and birefringence. It varies from cream to pinkish in color. The topaz occurs in two varieties, both rather unusual; one is as rounded cream-colored grains, composed of a submicroscopic aggregate resembling chert (pl. 6), the other as reddish-white mottled grains in which a columnar-aggregate structure is rarely seen. The spinel is a yellowish to greenish gahnite, sometimes showing octahedral faces. Tourmaline-quartz fels occurs sparingly and staurolite very rarely.

Table 22 gives the powder patterns of reddish-brown cryptocrystalline topaz from the batelle concentrate and a standard (XPDF 12-765) pattern of topaz (average of Brazilian, Mexican, and Utah topazes). Table 23 gives the chemical analyses of this topaz and of similar chert-like topaz from South Carolina (referred to below).

TABLE 22.—X-ray powder data for topaz

X-ray film 678 Guvana ¹		X-ray film 687 Guyana ²		Average of topaz from Brazil, Mexico, and Utah ³ XPDF 12-765		
<i>I</i> ⁴	<i>d</i>	<i>I</i> ⁴	<i>d</i>	<i>I</i>	<i>d</i>	<i>hkl</i>
vw	4.429	vw	4.418	5	4.395	020
w	4.151	w	4.150	4	4.194	200
				11	4.111	011
				6	3.896	120
vw	3.914	vw	3.921	60	3.693	111
vvs	3.712	vvs	3.702			
s	3.538	vw	3.562			
		vw	3.349			
vvs	3.216	vvs	3.205	66	3.195	021
s	3.039	vw	3.035	37	3.037	220
				23	2.986	121
vs	2.943	vvs	2.935	100	2.937	211
		vw	2.697			
vs	2.495	s	2.489	22	2.4804	031
				10	2.3966	301
vs	2.379	s	2.368	26	2.3783	131
vw	2.357			45	2.3609	320
				8	2.3247	002
		vw	2.312	9	2.3130	311
vw	2.256	vw	2.255	6	2.2470	012
ms	2.237	vw	2.207	10	2.1989	040
ms	2.176	vw	2.176	12	2.1711	112
				8	2.1269	140
s	2.108	vs	2.104	44	2.1049	321
vvs	2.064	s	2.060	24	2.0555	022
w	1.996	vw	1.991	7	1.9872	041
				9	1.9816	212
w	1.945	vw	1.946	4	1.9470	240
w	1.900			5	1.9340	141
ms	1.862	vs	1.867	24	1.8691	411
				26	1.8553	331
ms	1.828	vw	1.829	12	1.8212	032
ms	1.793	vw	1.805	8	1.7969	241
		vw	1.784	5	1.7796	132
vw	1.702					
vs	1.677	s	1.676	27	1.6706	232
vw	1.659	vw	1.659	8	1.6561	322
w	1.628	vw	1.626	11	1.6203	341
vw	1.605	vw	1.603	2	1.6014	431
				3	1.5974	042
vw	1.576	vw	1.577	1	1.5791	501
				3	1.5684	142, 520
				<1	1.5573	402

TABLE 22.—X-ray powder data for topaz—Continued

X-ray film 678 Guyana ¹		X-ray film 687 Guyana ²		Average of topaz from Brazil, Mexico, and Utah ³ XPDF 12-765			
<i>l</i> ⁴	<i>d</i>	<i>l</i> ⁴	<i>d</i>	<i>l</i>	<i>d</i>	<i>hkl</i>	
					1	1.5544	511
					4	1.5491	003
s	1.533	s	1.534	12	1.5335	412	
				16	1.5264	031, 332	
				6	1.5180	440	
		vvw	1.506	<1	1.5006	113	
				2	1.4296	242	
		vvw	1.488	3	1.4860	521	
s	1.467	vvw	1.470	5	1.4647	060	
				9	1.4614	023	
w	1.451	vvw	1.450	8	1.4433	160, 441	
					1.4398	123	
vs	1.425	s	1.425	4	1.4344	213	
vs	1.410	mw	1.412	26	1.4180	351	
vvw	1.391	mw	1.398	25	1.4023	052	
		mw	1.381				
vs	1.361	s	1.362				
		vvw	1.349				
vw	1.336	vvw	1.335				
vw	1.306	vvw	1.307				
vvw	1.286	vvw	1.285				
mw	1.260	vvw	1.260				
vvw	1.250						
		vvw	1.239				
mw	1.221	vvw	1.222				
vvw	1.209	vvw	1.209				
mw	1.170						
mw	1.149						

¹ Light flesh-colored rounded grains of topaz, Director Creek, Guyana.² Reddish-brown topaz, Director Creek, Guyana.³ Swanson and others (1962).⁴ vvs, very very strong; vs, very strong; s, strong; ms, moderately strong; mw, moderately weak; w, weak; vw, very weak; vvw, very very weak.

TABLE 23.—Analysis of topaz

Constituent	Guyana ¹ (percent)	South Carolina ² (percent)
Al ₂ O ₃	³ 55.2	56.76
TiO ₂	⁴ 0.47	
SiO ₂	³ 32.7	33.00
—H ₂ O	⁵ 0.12	0.04
+H ₂ O	² 2.8	2.67
F	⁶ 15.1	13.23
Fe ₂ O ₃		trace
Total C as CO ₂	⁵ 0.35	
Sub total	106.74	105.70
Less O equivalent of F	6.36	5.57
Total	100.38	100.13
Specific gravity ⁷	3.55	3.509

¹ Blanche Ingram, U.S. Geological Survey, analyst; Claude Waring, U.S. Geological Survey, determined (spectrographically) Fe 0.03 percent, Mg 0.01 percent.² Pardee, Glass, and Stevens, 1937.³ The sample (2 mg) was fused with NaOH, and the solution from the fusion was used to determine Al₂O₃ and SiO₂ spectrophotometrically. Al₂O₃ was determined with alizarin red S and SiO₂ as the molybdenum blue complex. The amount of F in the aliquot used for measurement of Al₂O₃ was below the interference level.⁴ The sample (approximately 25 mg) was fused with Na₂CO₃ and dissolved in perchloric acid; Ti was determined spectrophotometrically with Tiron.⁵ The sample (100 mg) was heated at 110°C to constant weight to determine —H₂O. The sample was then mixed with twice its weight of freshly fused sodium tungstate, and +H₂O and total C were determined by igniting the sample at 900°C in a tube combustion furnace. The tube contained MgO in the packing to retain F. H₂O and CO₂ were absorbed and weighed.⁶ F was determined by a specific ion-electrode procedure. Samples of 10 mg each were decomposed by fusing with Na₂CO₃-ZnO, and the F was leached with H₂O. Measurement of F was made in a 0.5 M sodium citrate solution to prevent Al interference.⁷ Specific gravity was determined using a specific gravity bottle and toluene as liquid.

Cryptocrystalline detrital topaz, either cream-colored or reddish, does not appear to have been previously noted elsewhere in Guyana and according to Dr. Leandert Krook of the Surinam Geological and Mining Service (written commun., 1970), is unknown after many years of detrital-sediment study in Surinam. In both countries, however, the normal variety of topaz is a fairly common detrital mineral. Dr. D. Bleackley, of the Institute of Geological Sciences, London, notes that the cryptocrystalline topaz could well have been misidentified as gorceixite (written commun., 1969).

In all observable respects, the cream-colored or reddish topaz resembles a cryptocrystalline topaz described by Pardee and others (1937) from quartz veins in the Brewer gold mine in South Carolina. This topaz contained the highest H₂O (2.71 percent) and the lowest fluorine (13.23 percent) ever reported.

This cream-colored or reddish cryptocrystalline topaz appears to occur only with the merumite; it has not been found in the overlying local White Sand nor in the underlying altered volcanic ash. Clear transparent well-crystallized topaz is found else-

where in many Guyana localities, but the reddish and cream-colored cryptocrystalline varieties are not.

This topaz may have been mistaken for gorceixite; Dixon (1957) states that a report on merumite by Smith Bracewell to the Hon. Colonial Secretary, September 17, 1945, referred to the "abundance of gorceixite." Gorceixite, however, is known to occur elsewhere in Guyana.

CRYSTALLOGRAPHIC RELATIONSHIPS OF CrOOH COMPOUNDS

As already mentioned, the three mineral polymorphs of CrOOH, guyanaite, bracewellite, grimaldiite, and the fourth, an artificial compound not known as a mineral, have interesting crystallographic relationships to other metallic oxyhydroxides with composition ROOH. These relationships are indicated in table 24, which is an amplification of data in Strunz (1970).

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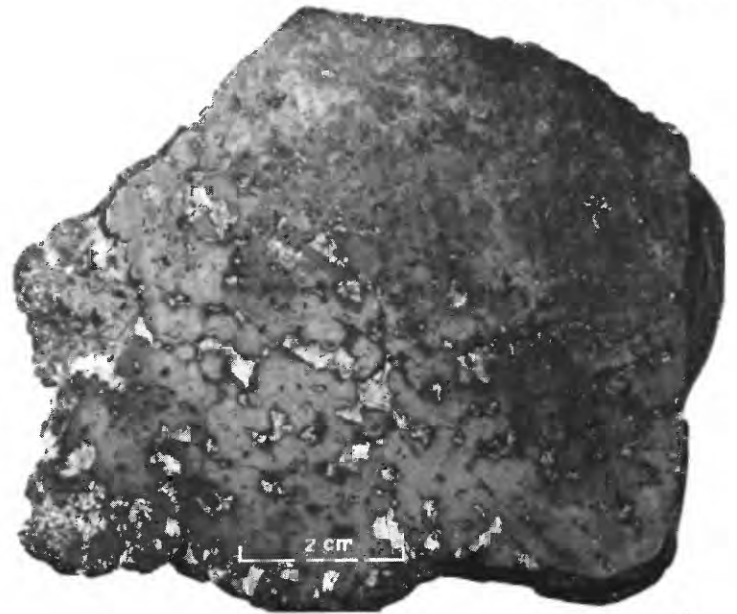
PLATES 1-6

PLATE 1

- FIGURE 1. Very large (8 cm) specimen of merumite. Exterior view showing botryoidal surface and inclusions of quartz.
2. Sawed face of merumite specimen in fig. 1 showing quartz inclusions.
 3. Exterior view of another very large (8 cm) merumite specimen showing botryoidal surface and quartz inclusions. Note that some of the quartz inclusions are well crystallized.
 4. Sawed face of merumite specimen in fig. 3 showing quartz inclusions and several areas of grimaldiite-mcconnellite (mottled areas indicated by arrows).



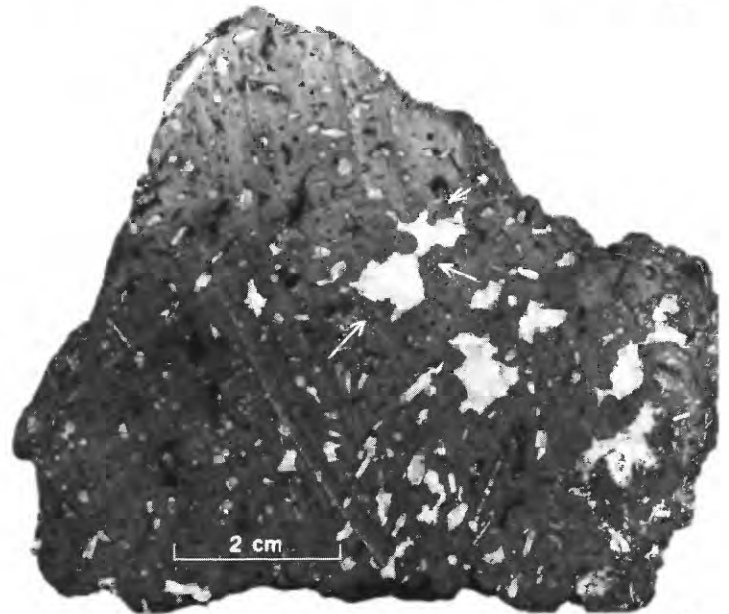
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3



4

PLATE 2

- FIGURE 1. Photomicrograph of a thin section of merumite with green subhedral eskolaite enclosing yellow-brown guyanaite. Plain transmitted light.
2. Thin section of merumite showing banded green eskolaite and yellow-brown guyanaite. Plain transmitted light.
 3. Thin section of merumite consisting almost entirely of guyanaite with very little eskolaite. Most of the guyanaite occurs in extremely fine-grained spheroidal aggregates, but coarse prismatic guyanaite is also present (see fig. 4). Plane-polarized light.
 4. Detail of fig. 3 showing both the coarse prismatic and fine-grained habits of guyanaite. Plane-polarized light.

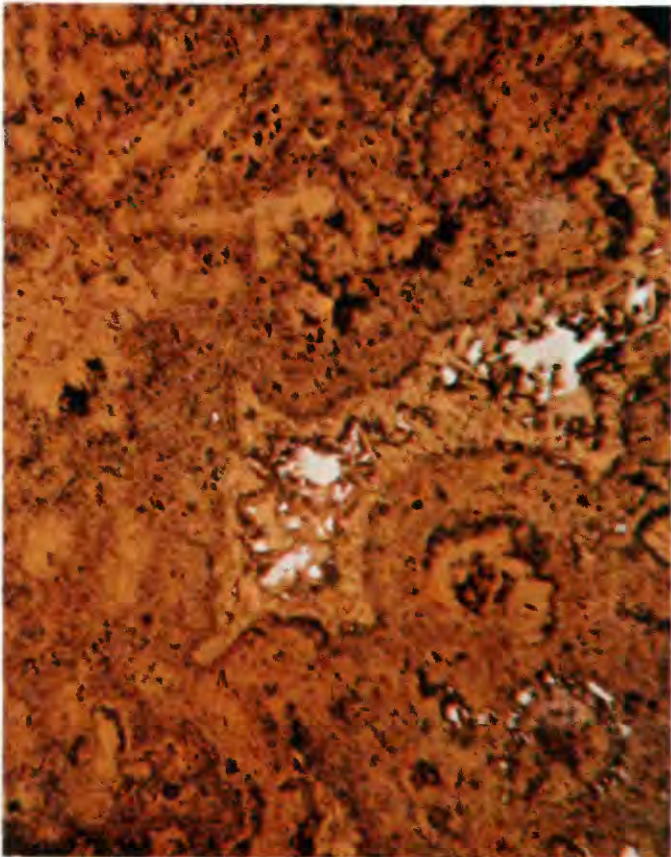


1

0.1 mm



2



3

0.1 mm

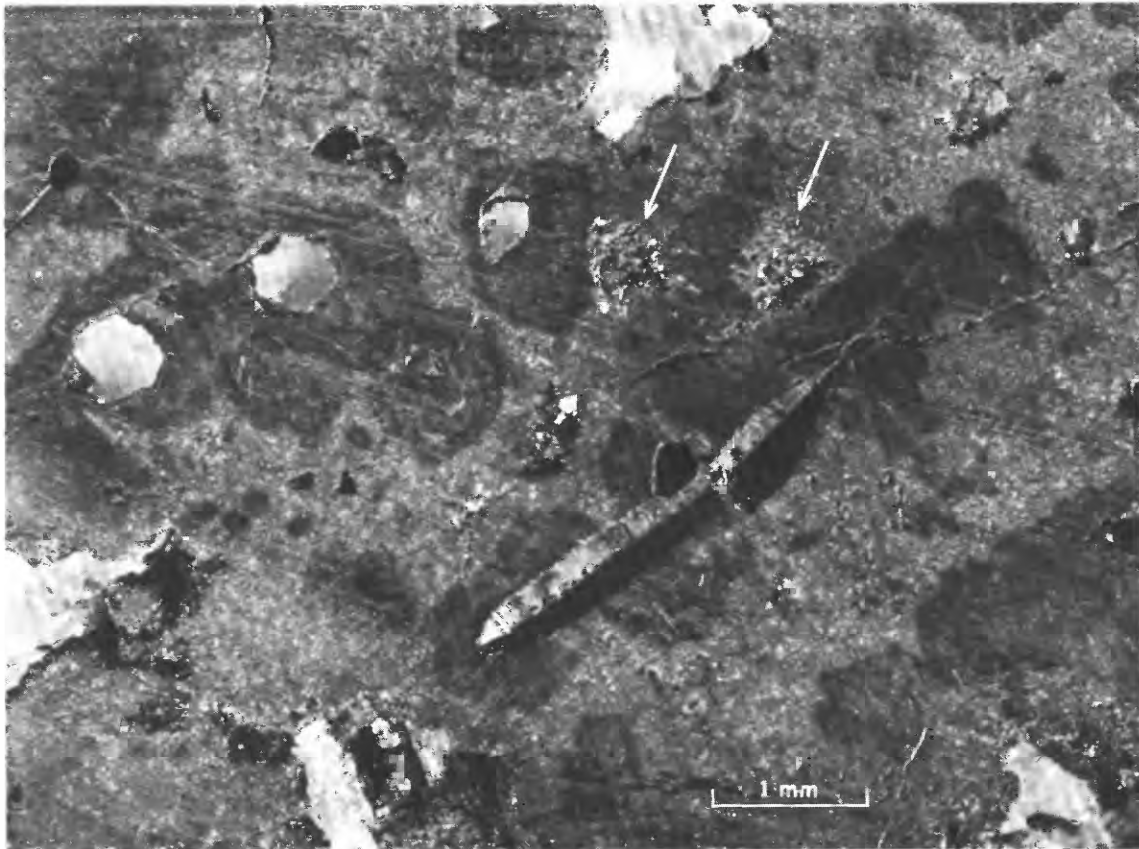


4

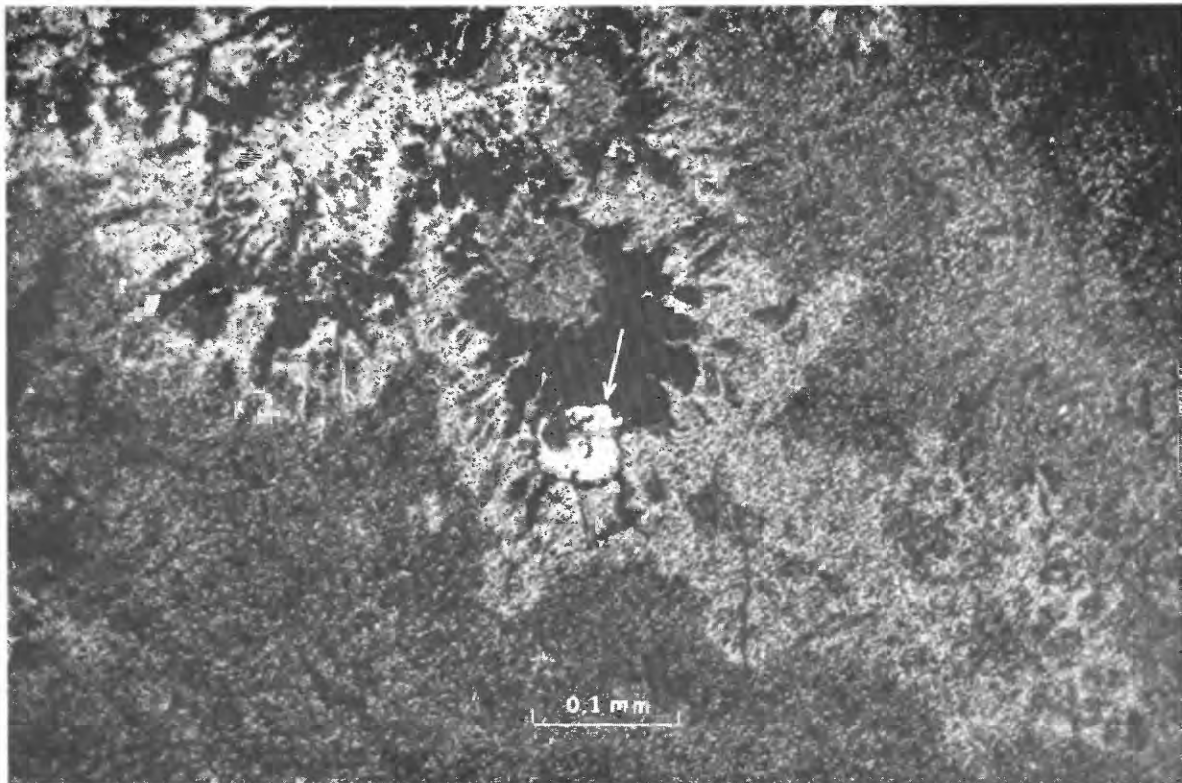
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PLATE 3

- FIGURE 1.** Polished surface of merumite showing quartz inclusions (note broken crystal) and mottled areas (indicated by arrows) which are granular aggregates of grimaldiite-mcconnellite polycrystals. Reflected light.
2. Polished section of merumite showing gold (at arrow). Reflected light.



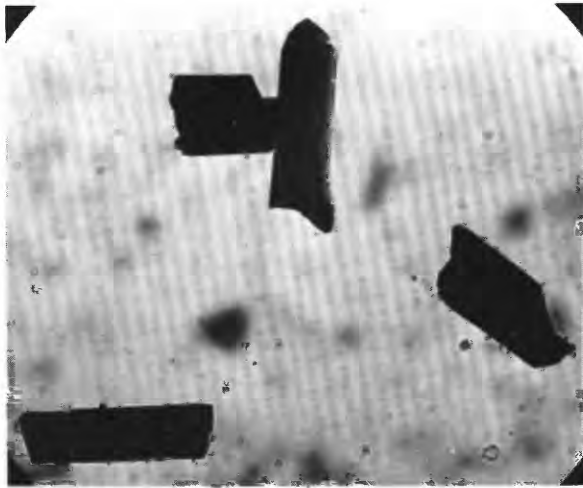
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2

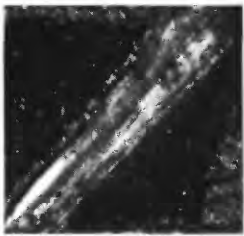
PLATE 4

- FIGURE 1. Bracewellite crystals (deep brown, almost black), showing prismatic habit, from vugs within merumite. Plain transmitted light.
2. Electron-probe analyses of two grimaldiite-mcconnellite polycrystals. *A* and *D*, Electron-probe photomicrographs of the edges of two specimens. Width of each edge is approximately 70 μm . *B* and *E*, Scanning X-rays images in $\text{CrK}\alpha$ radiation showing distribution of chromium in specimens *A* and *D*, respectively. *C* and *F*, Scanning X-ray images in $\text{CuK}\alpha$ radiation showing distribution of copper in specimens *A* and *D*, respectively.



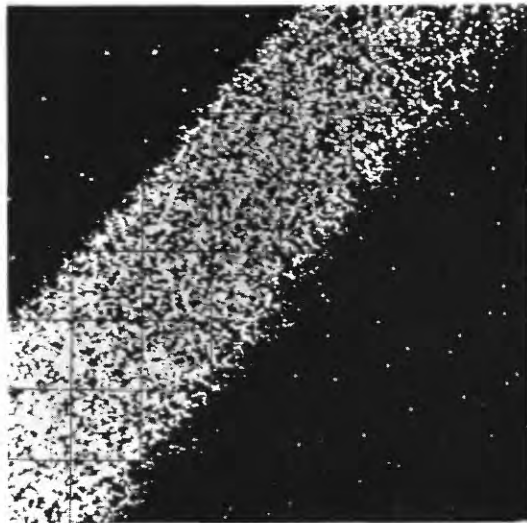
1

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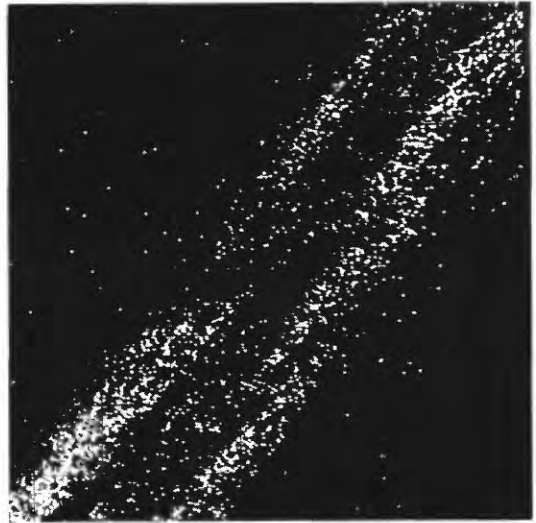
2A

70 μ m



2B

70 μ m



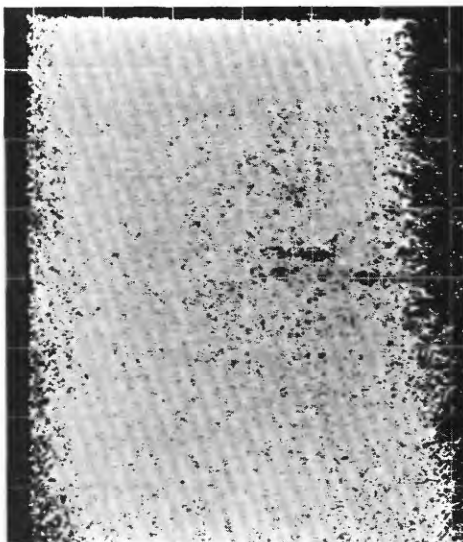
2C

70 μ m



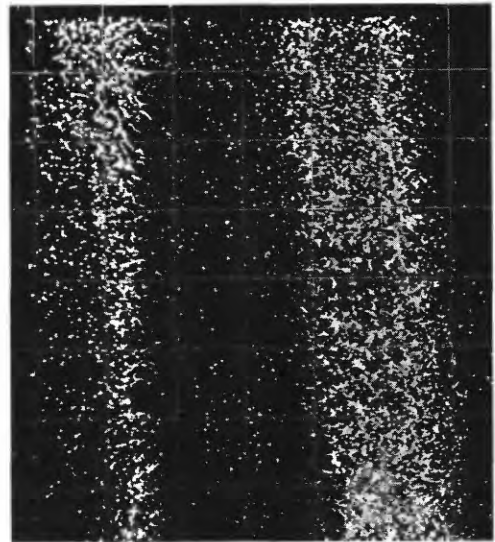
2D

70 μ m



2E

70 μ m



2F

70 μ m

PLATE 5

- FIGURE 1. Scanning-electron photomicrograph of a grimaldiite-mcconnellite polycrystal.
Taken by A. J. Tousimis.
2. Scanning-electron photomicrograph of octahedral crystals of chromian gahnite and a flake of grimaldiite-mcconnellite (upper left). Edge of octahedron (upper right) is 35 μm . Taken by A. J. Tousimis.

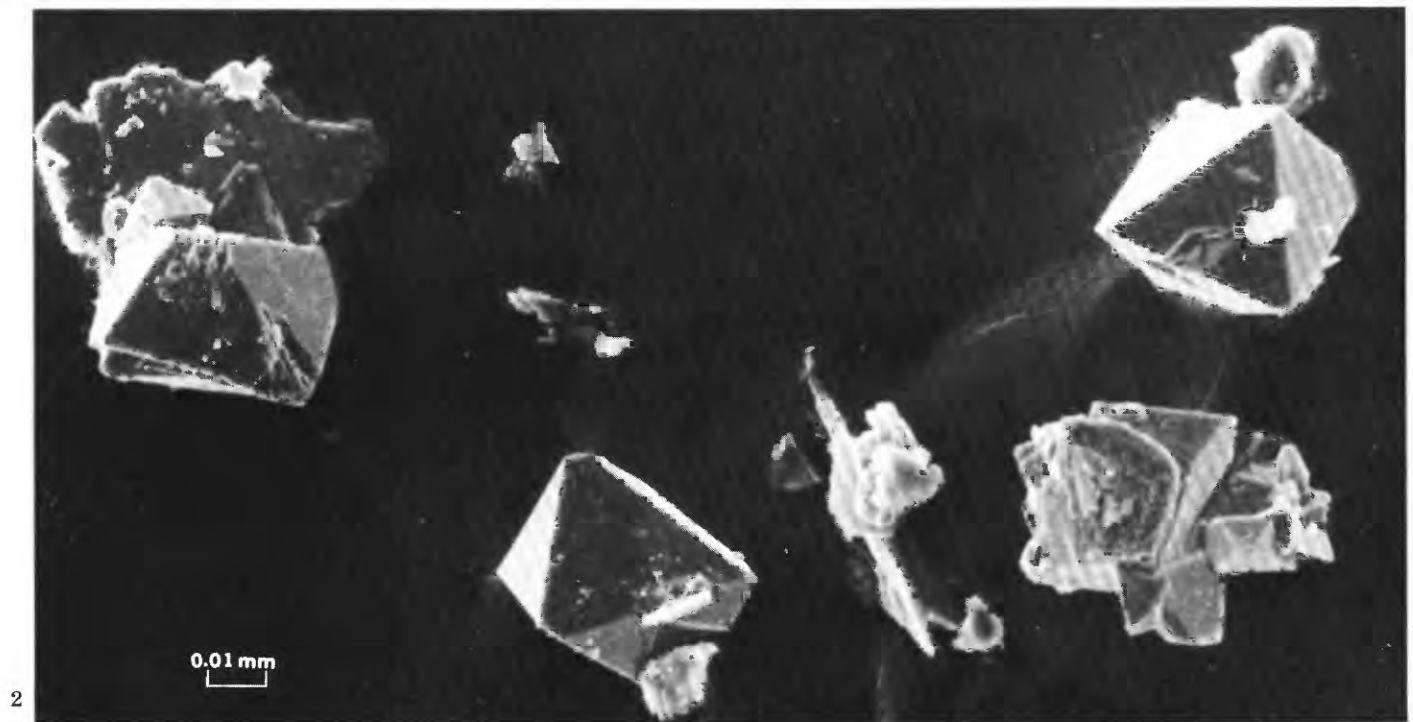
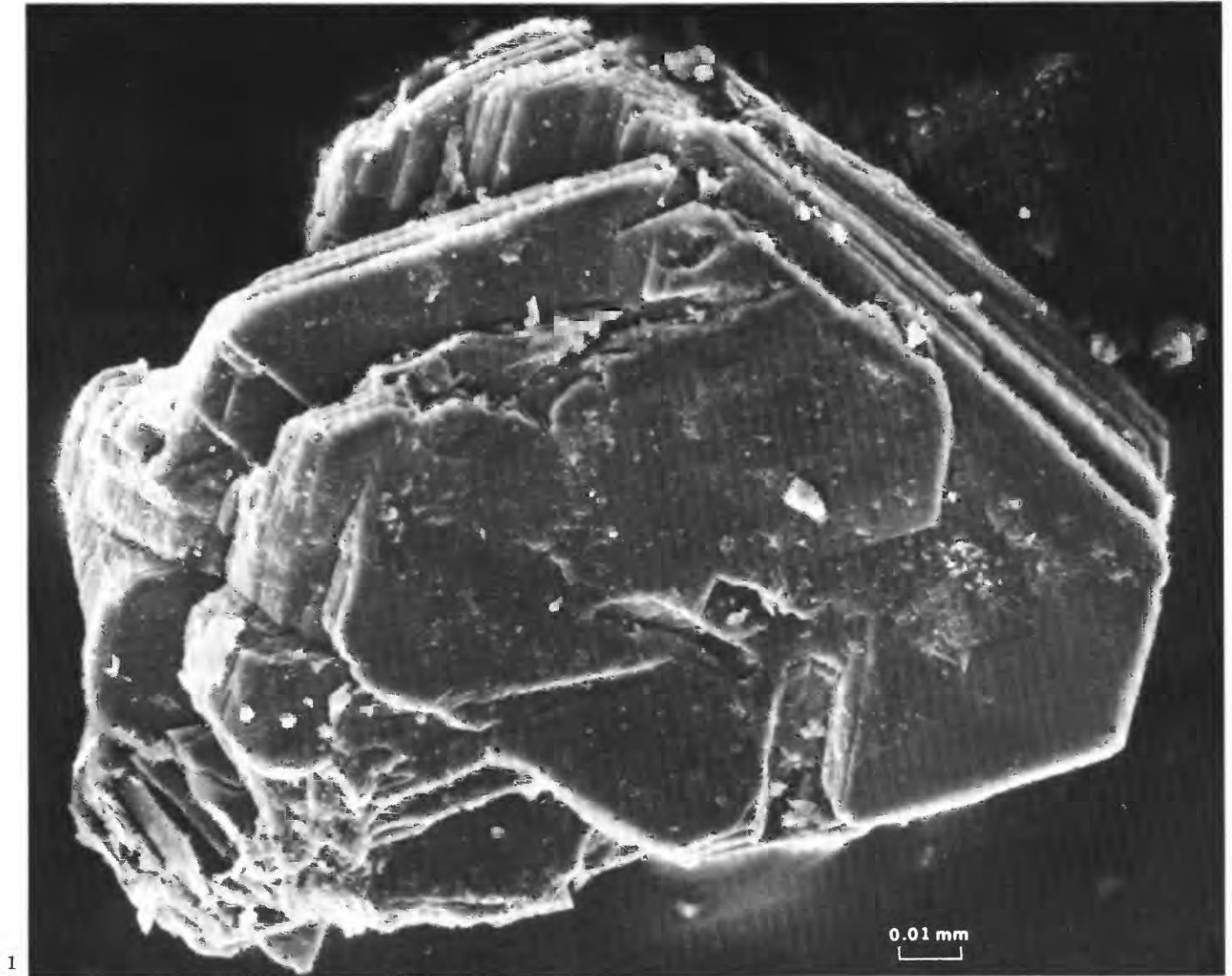
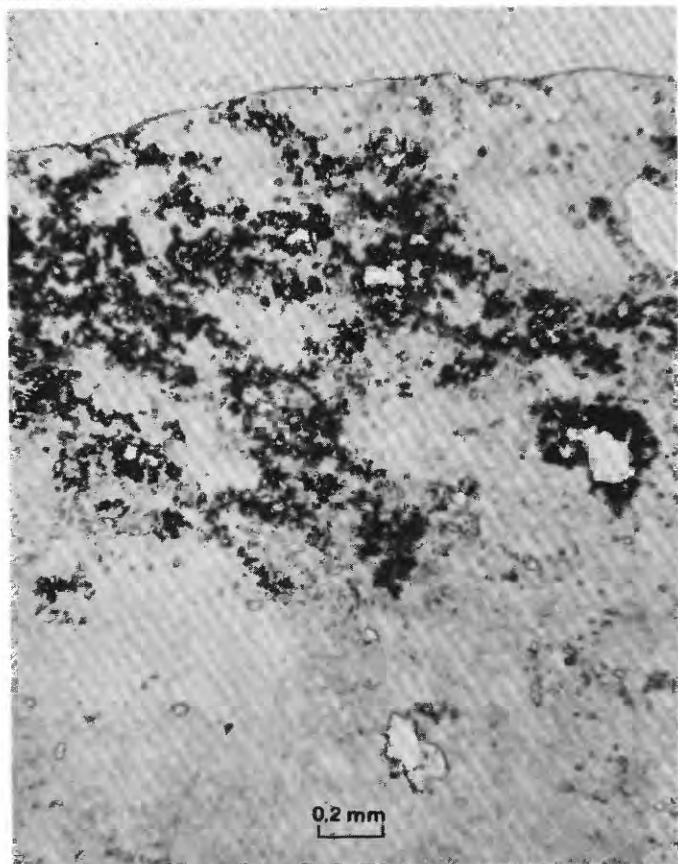


PLATE 6

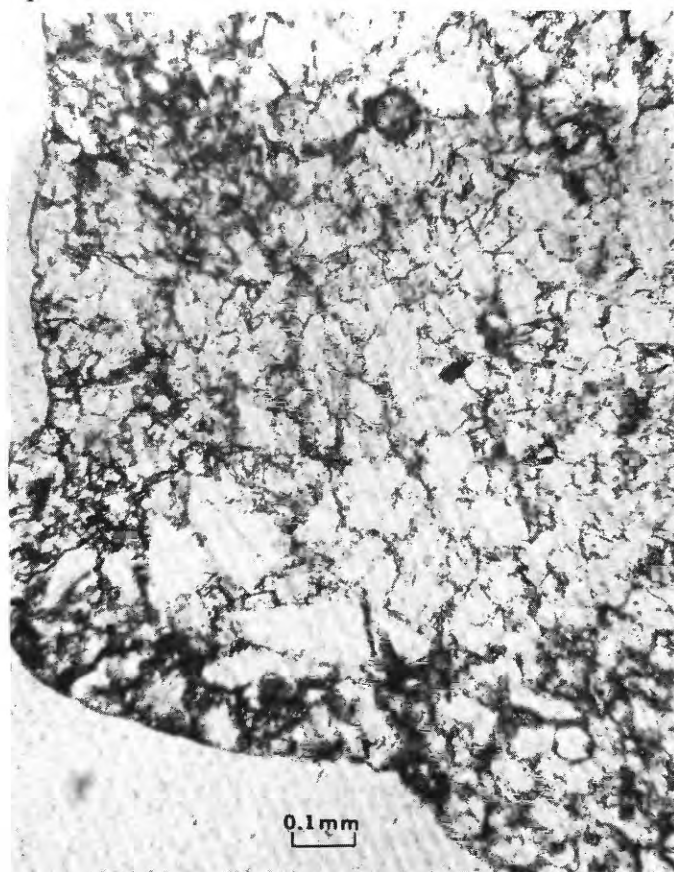
- FIGURES 1, 2. Photomicrographs of topaz showing structure of fine-grained aggregate.
Fig. 1 taken in plane-polarized light and fig. 2 with crossed polarizers.
- 3, 4. Another thin section of a topaz aggregate. Fig. 3 taken in plane-polarized light and fig. 4 with crossed polarizers.



1



2



3



4