

# Merumite—A Complex Assemblage of Chromium Minerals from Guyana

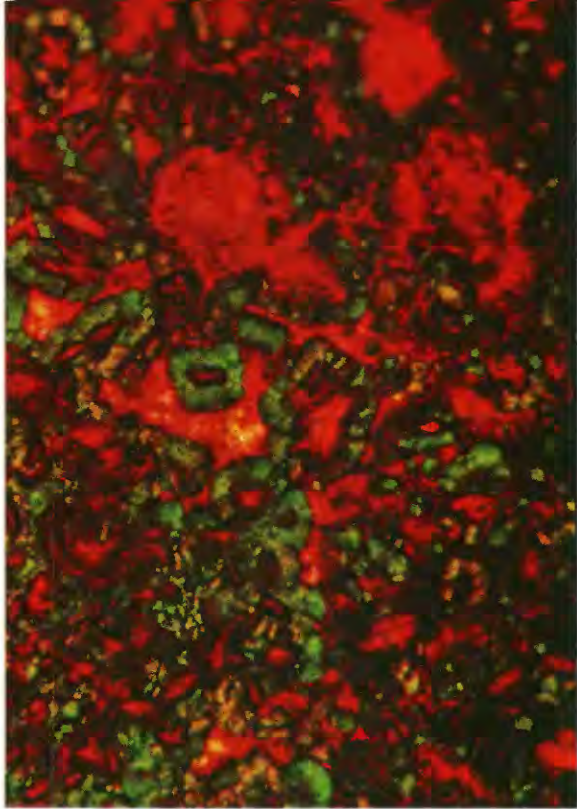
---

GEOLOGICAL SURVEY PROFESSIONAL PAPER 887

*Prepared in cooperation with  
the Geological Survey of Guyana*



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



0.1 mm



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 guyanaitite.

UPPER RIGHT: Banded structure of green eskolaite and yellow to brown guyanaitite. 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 guyanaitite showing banded structure.

# Merumite—A Complex Assemblage of Chromium Minerals from Guyana

By CHARLES MILTON, D. E. APPLEMAN, M. H. APPLEMAN,  
E. C. T. CHAO, FRANK CUTTITTA, J. I. DINNIN,  
E. J. DWORNIK, B. L. INGRAM, and H. J. ROSE, JR.

---

GEOLOGICAL SURVEY PROFESSIONAL PAPER 887

*Prepared in cooperation with  
the Geological Survey of Guyana*



UNITED STATES DEPARTMENT OF THE INTERIOR

THOMAS S. KLEPPE, *Secretary*

GEOLOGICAL SURVEY

V. E. McKelvey, *Director*

---

Library of Congress Cataloging in Publication Data

Main entry under title:

Merumite—a complex assemblage of chromium minerals from Guyana.

(Geological Survey professional paper 887)

Bibliography: p.

Supt. of Docs. no.: I 19.16:887

1. Merumite—Guyana. I. Milton, Charles, 1896– II. Series: United States. Geological Survey. Professional paper 887.

QE391.M45M47 549'.7 74-16247

---

For sale by the Superintendent of Documents, U.S. Government Printing Office  
Washington, D.C. 20402 (Paper cover)  
Stock No. 024-001-02872-7/Catalog No. I 19.16:887

# 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) |      | $\gamma$ -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 |
|---|------|
| <b>FIGURE</b> 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 |
|--|------|
| <b>TABLE</b> 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 $\text{Cr}_2\text{O}_3$ ..... | 9    |
| 5. Cell constants of guyanaite (from Guyana and Finland), and of $\text{CrOOH}$ , $\text{ScOOH}$ , and $\text{InOOH}$ .....  | 11   |
| 6. Analyses of guyanaite .....   | 12   |
| 7. X-ray powder data of $(\text{Cr}, \text{Al}, \text{Fe}, \text{Ti}, \text{Mn})\text{O}_2$ from guyanaite, and $\text{CrO}_2$ from $\text{CrOOH}$ .....   | 13   |
| 8. X-ray powder data of $(\text{Cr}, \text{Al}, \text{Fe}, \text{Ti Mn})_2\text{O}_3$ .....  | 13   |
| 9. X-ray powder data of guyanaite (from Guyana and Finland), "merumite" and synthetic guyanaite $\text{CrOOH}$ .....   | 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 $\text{CrOOH}$ compounds and other metallic hydroxides .....  | 27   |

# MERUMITE—A COMPLEX ASSEMBLAGE OF CHROMIUM MINERALS FROM GUYANA

By CHARLES MILTON, D. E. APPLEMAN, M. H. APPLEMAN, E. C. T. CHAO, FRANK CUTTITTA, J. I. DINNIN,  
E. J. DWORNIK, B. L. INGRAM, and H. J. ROSE, JR.

## ABSTRACT

Merumite, found as black grains or pebbles in a small stream bed in Guyana, is a complex assemblage of hexagonal eskolaite (predominant), essentially  $\text{Cr}_2\text{O}_3$ ; guyanaite and bracewellite, both orthorhombic and essentially  $\text{CrOOH}$ ; grimaldiite, rhombohedral and also essentially  $\text{CrOOH}$ ; and mcconnellite, rhombohedral  $\text{CrOOCu}$ , 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  $\text{Cr}_2\text{O}_3$ . 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,  $\text{Cr}_2\text{O}_3$ , 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.<sup>1</sup> 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  $60^\circ$  W., lat  $6^\circ$  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 Ridge<sup>2</sup>, which consists of Roraima-like sandstones, conglomerates, and volcanic ash, with dips of  $30^\circ$  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 Matthews<sup>3</sup>. 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

<sup>1</sup> Named for Murray R. Director, who examined the merumite deposit in 1957.

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

<sup>3</sup> 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.

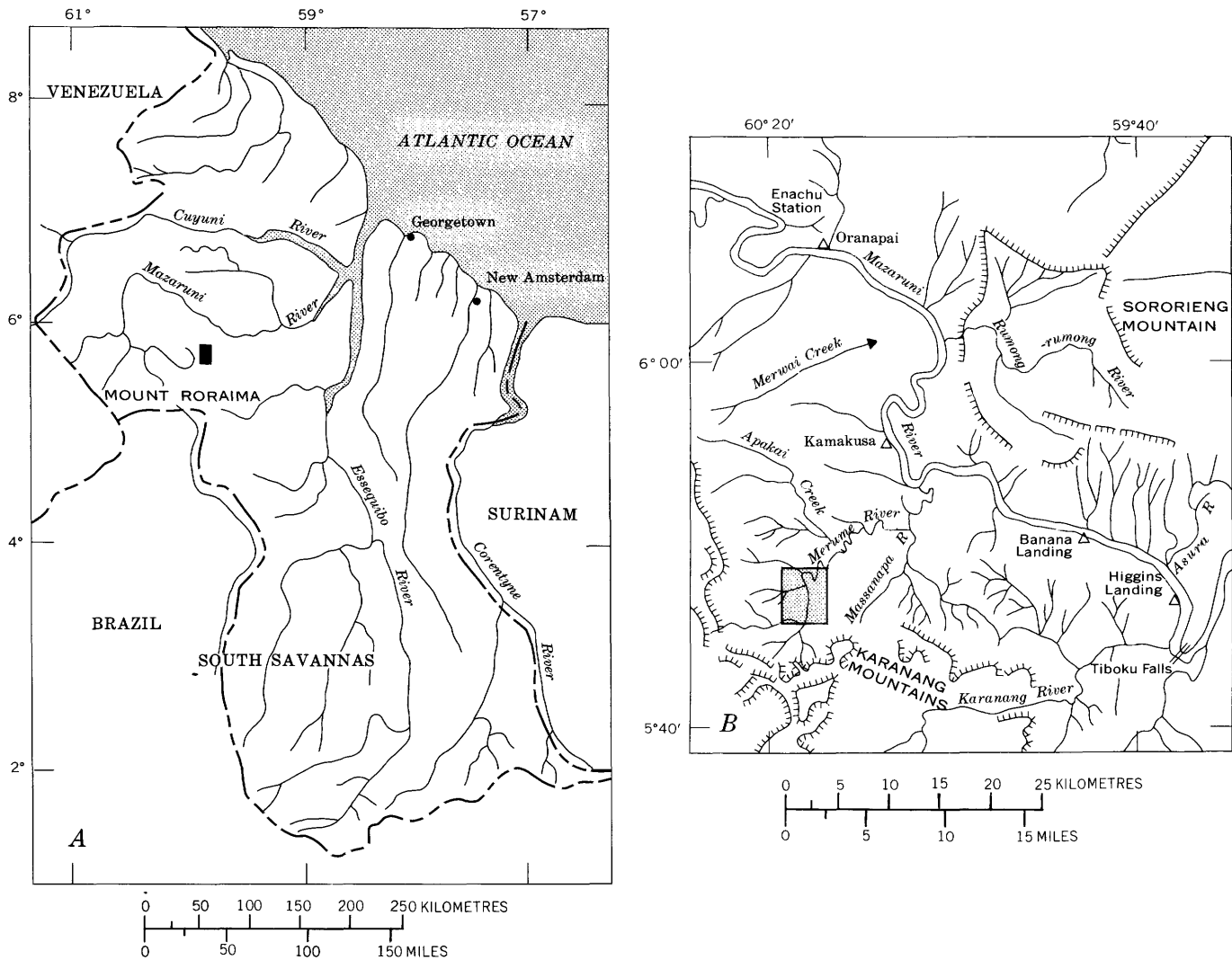


FIGURE 1.—Index maps showing A, location of merumite-bearing area (shaded) in Guyana, and B, enlarged view of merumite-bearing area (shaded) and surrounding region. Merumite-bearing area is shown in greater detail on figure 2. Escarpments are shown in B by hachured lines.

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-

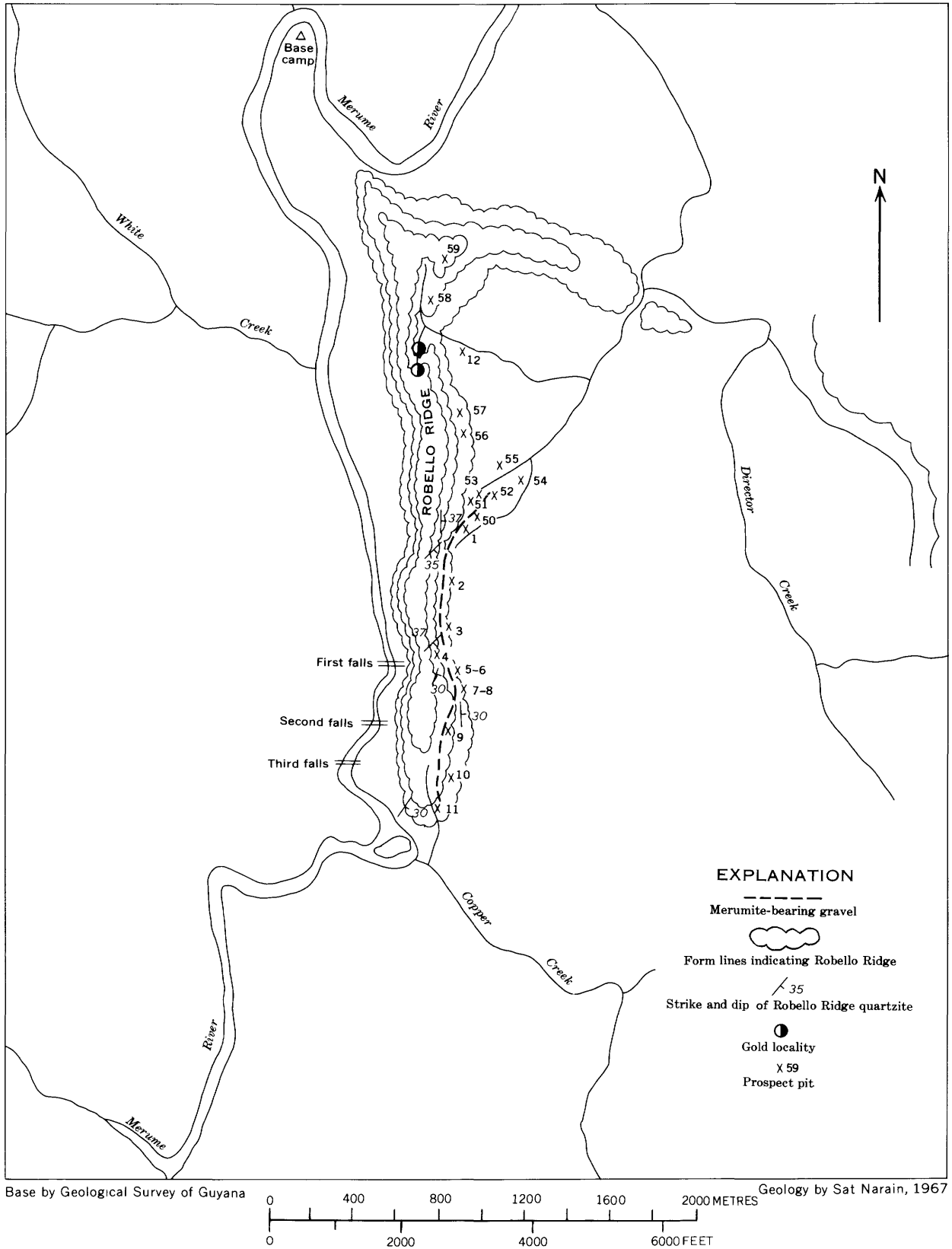












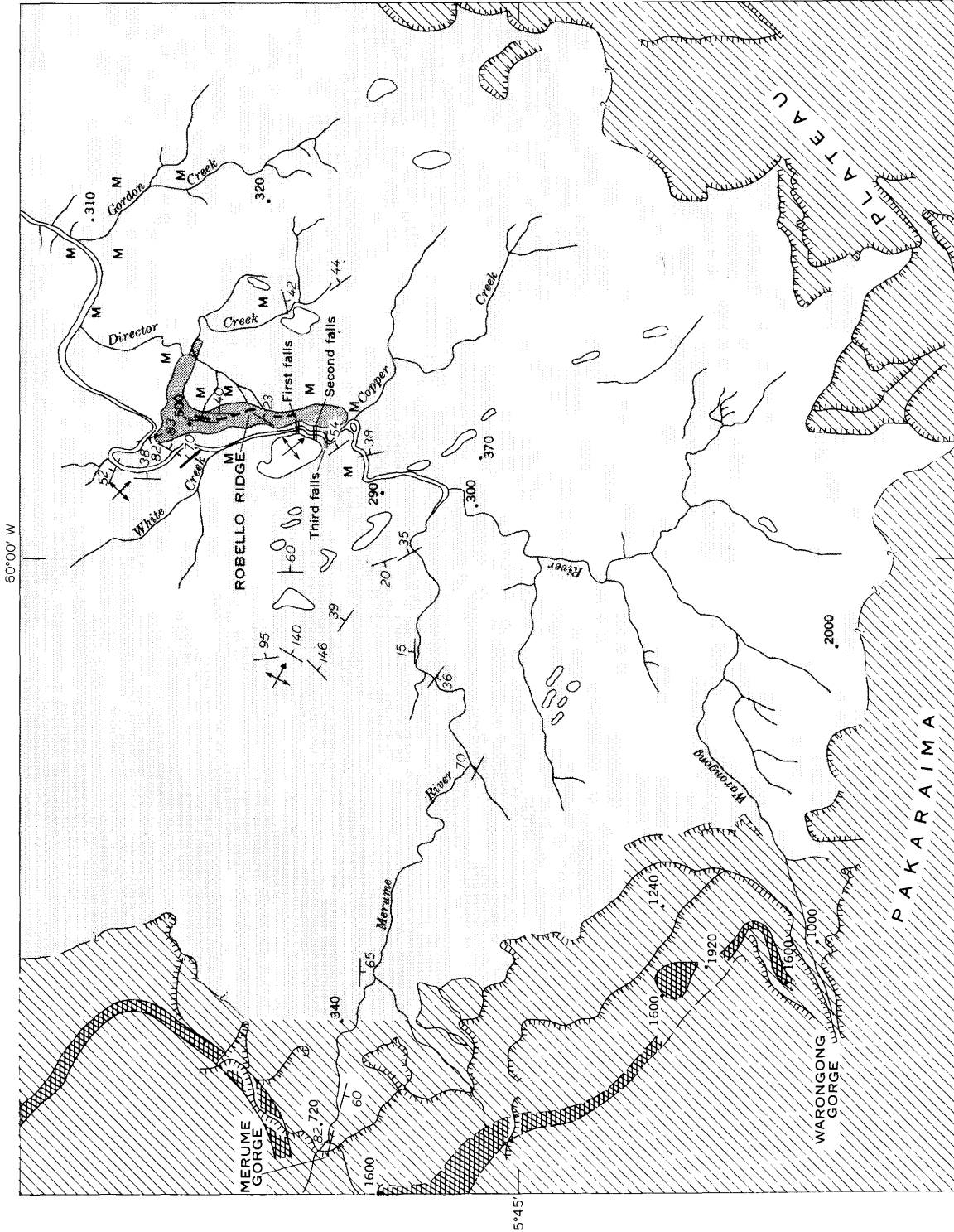


FIGURE 2.—Sketch map of the Merume River area showing the location of the merumite deposit. Area of this map is shaded on figure 1.

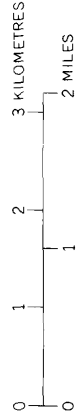
MERUMITE

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/m<sup>3</sup>. 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  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{Mn}_2\text{O}_3$ , and  $\text{V}_2\text{O}_5$ , which generally appear in the chemical analyses of merumite and its constituent minerals, is one of general partial substitution for the dominant  $\text{Cr}_2\text{O}_3$ . There are indeed, as will be seen, specific minerals characterized by major  $\text{Al}_2\text{O}_3$ : 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  $\text{Al}_2\text{O}_3$ -containing minerals.

#### ISOTOPIC STUDY

Svec and others (1962) studied the relative abundance of the chromium isotopes  $\text{Cr}^{50}$ ,  $\text{Cr}^{52}$ ,  $\text{Cr}^{53}$ , and  $\text{Cr}^{54}$  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  $\text{Cr}_2\text{O}_3$ .

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 <sup>1</sup>        | B <sup>2</sup> | C <sup>3</sup> |
| $\text{Cr}_2\text{O}_3$ -----            | 81.30                 | 76.74          | 80.28          |
| $\text{Al}_2\text{O}_3$ -----            | 6.55                  | 6.82           | ----           |
| $\text{Fe}_2\text{O}_3$ (total Fe) ----- | 1.58                  | 5.91           | 2.10           |
| $\text{TiO}_2$ -----                     | .75                   | 1.40           | ----           |
| $\text{V}_2\text{O}_5$ -----             | .15                   | .15            | ----           |
| $\text{MnO}$ -----                       | .06                   | .06            | ----           |
| $\text{H}_2\text{O}^-$ -----             | .10                   | .11            | ----           |
| $\text{H}_2\text{O}^+$ -----             | 8.08                  | 8.25           | ----           |
| $\text{SiO}_2$ -----                     | 1.30                  | .95            | 1.78           |
| $\text{MgO}$ -----                       | 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           | ----           |

<sup>1</sup> 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).

<sup>2</sup> 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.

<sup>3</sup> 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<br>(in percent) |
|---|------------------------|
| <b>MERUMITE<sup>1</sup> (ESKOLAITE, 37 PERCENT; GUYANAITE, 63 PERCENT)<br/>ANALYSIS A<sup>2</sup></b> |                        |
| Cr <sub>2</sub> O <sub>3</sub> -----  | 88.8                   |
| Al <sub>2</sub> O <sub>3</sub> -----  | 3.1                    |
| CaO -----   | .1                     |
| H <sub>2</sub> O -----  | 2.3                    |
| Ignition loss -----   | (3.5)                  |
| Total -----   | 94.3                   |
| <b>ANALYSIS B<sup>3</sup></b>   |                        |
| Cr <sub>2</sub> O <sub>3</sub> -----  | 89.2                   |
| <b>ANALYSIS C<sup>4</sup></b>   |                        |
| 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                    |

<sup>1</sup> This specimen was analyzed to test analytical procedures for similar quantities.

<sup>2</sup> 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 H<sub>2</sub>O and the distribution of Al<sub>2</sub>O<sub>3</sub>, and so forth, between eskolaite and guyanaite. With 6.8 percent H<sub>2</sub>O (the maximum derived from 89.2 percent Cr<sub>2</sub>O<sub>3</sub> and 4.0 percent Al<sub>2</sub>O<sub>3</sub>, and so forth) and all Al<sub>2</sub>O<sub>3</sub>, and so forth, in guyanaite, a composition of 38 percent eskolaite and 62 percent guyanaite follows; and with all Al<sub>2</sub>O<sub>3</sub>, 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<br>(in percent)             |
|--|------------------------------------|
| <b>ANALYSIS C<sup>1</sup> (SPECTROGRAPHIC)<br/>MERUMITE<sup>1</sup> (ESKOLAITE, 37 PERCENT; GUYANAITE, 63 PERCENT—Continued<br/>ANALYSIS C<sup>1</sup>—Continued</b> |                                    |
| K, P, B, Bi, Cd, Ce, Co, Ge,<br>Hf, Hg, In, La, Li, Pd, Pt,<br>Re, Sc, Sn, Ta, Te, Th, Ti, U,<br>W, Y, Yb, Zn, Zr.   | Looked for<br>but not<br>detected. |
| <b>MERUMITE (GUYANAITE PLUS ESKOLAITE)<br/>ANALYSIS D<sup>2</sup> (SPECTROGRAPHIC)</b>   |                                    |
| 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,<br>Zn, Cd, Zr, B, P, Ba, Sr, Y,<br>La, U, Th, Cb, W, Pt, Au.   | Looked for<br>but not<br>detected. |
| <b>ESKOLAITE<br/>ANALYSIS E<sup>3</sup></b>  |                                    |
| Cr <sub>2</sub> O <sub>3</sub> -----   | 94.13±0.20                         |
| Al <sub>2</sub> O <sub>3</sub> -----   | <sup>7</sup> 0.19                  |
| Fe <sub>2</sub> O <sub>3</sub> -----   | 0.55                               |
| V <sub>2</sub> O <sub>5</sub> -----  | 4.58                               |
| MgO -----  | <sup>7</sup> 0.03                  |
| MnO -----  | <sup>7</sup> 0.03                  |
| SiO <sub>2</sub> -----   | <sup>7</sup> 0.20                  |
| H <sub>2</sub> O -----   | 0.10                               |
| Total -----  | <sup>8</sup> 99.81                 |
| Density -----  | 5.18 measured<br>5.218 calculated. |

<sup>2</sup> 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 K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> standards.

| Weight sample (in mg) | Cr <sub>2</sub> O <sub>3</sub> (percent) |
|-----------------------|--|
| 1.98 -----            | 89.1                                     |
| 2.47 -----            | 89.4                                     |
| 2.47 -----            | 89.2                                     |

<sup>4</sup> 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.

<sup>5</sup> 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.

<sup>6</sup> Analyst, Jorma Kinnunen, in Kouvo and Vuorelainen (1958) who gave the formula, Cr<sub>11.90</sub>V<sub>0.05</sub>Fe<sub>0.05</sub>O<sub>3</sub>.

<sup>7</sup> Based on spectrographic analysis.

<sup>8</sup> 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<sup>1, 2</sup>  
[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  |

<sup>1</sup>“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.”  
<sup>2</sup> 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 Cr<sub>2</sub>O<sub>3</sub>, 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 Cr<sub>2</sub>O<sub>3</sub> (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 Cr<sub>2</sub>O<sub>3</sub>

| Merumite, film 16827 <sup>1</sup> |          | Merumite approaching eskolaite, film 16765 Guyana |       | Guyanaite, film 00188 Guyana (four strongest lines) |       | Eskolaite, Finland (Kouvo and Vuorelainen, 1958) |        |       | Cr <sub>2</sub> O <sub>3</sub> XPDF 6-0504 <sup>2</sup> |        |       |
|-----------------------------------|----------|---|-------|---|-------|--|--------|-------|---|--------|-------|
| I <sup>3</sup>                    | d        | I <sup>3</sup>                                    | d     | I <sup>3</sup>                                      | 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   |

<sup>1</sup> For analysis, see table 2.  
<sup>2</sup> X.P.D.F. 6-0504 refers to Index (Inorganic) to the Powder Diffraction File 1972, Joint Committee on Powder Diffraction Standards, Swarthmore, Penn.  
<sup>3</sup> 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  $\text{Cr}_2\text{O}_3$ ; almost all of the remaining 6 percent is  $\text{V}_2\text{O}_5$  of very similar molecular weight. The Guyana eskolaite, however, may vary from almost wholly  $\text{Cr}_2\text{O}_3$  with very minor  $\text{Al}_2\text{O}_3$  (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  $\text{Cr}_2\text{O}_3$  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  $\text{Cr}_2\text{O}_3$  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  $5.035 \pm 0.1755$ .

#### GUYANAITE

##### OCCURRENCE IN GUYANA AND FINLAND, AND SYNTHESIS

Tombs and others (1964) synthesized orthorhombic  $\text{CrOOH}$  with unit cell dimensions  $a=4.861$  Å,  $b=4.292$  Å, and  $c=2.960$  Å (table 5) by heating  $\text{CrO}_2$  in water at  $450^\circ\text{C}$  under a total pressure of 40,000 lb/in<sup>2</sup> 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 <sup>-3</sup> ) | 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>P<sub>2</sub>nm</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  $\gamma$ -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

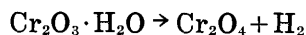
Table 6 gives a microchemical analysis (37 mg) of guyanaite crystals from Guyana and the analysis of guyanaite from Finland by Vuorelainen and others (1968). An analysis of merumite consisting of about two-thirds guyanaite and one-third eskolaite is given in table 2 (analyses A-C).

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

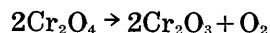
positions closer to  $2\text{Cr}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , as proposed by Vuorelainen and others (1968), than to  $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , which is known to be correct on the basis of the single-crystal X-ray data. The reason for this difference may be explained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

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

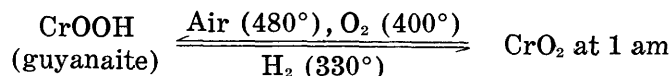
at about  $335^\circ\text{C}$



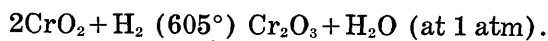
at about  $1,000^\circ\text{C}$



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



and the irreversible reaction:



Thus, in a Penfield determination of  $\text{H}_2\text{O}^+$  in guyanaite, there is a loss of hydrogen initially with formation of  $\text{CrO}_2$  instead of simple dehydration with formation of  $\text{Cr}_2\text{O}_3$ . If this hydrogen is lost, then  $\text{CrO}_2$  may remain unreduced to  $\text{Cr}_2\text{O}_3$  and the  $\text{H}_2\text{O}$  weighed may represent less than the whole  $\text{H}_2\text{O}$  in  $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$  ( $\text{CrOOH}$ ); 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  $\text{H}_2\text{O}$  was found,

whereas 14.3 percent is required for a formula  $\text{ROOH}$ .

The determination of loss on ignition should give a correct figure for water, provided that all the  $\text{Cr}_2\text{O}_4$  is completely converted to  $\text{Cr}_2\text{O}_3$  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  $\text{H}_2\text{O}$  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 | $\text{Cr}_2\text{O}_3$ | 63.5    |
|           | $\text{CrOOH}$          | 28.3    |
| guyanaite | $\text{AlOOH}$          | 3.6     |
| Total     |                         | 95.4    |

If the X-ray fluorescence determination of  $\text{Cr}_2\text{O}_3$ , 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  $\text{CaO}$ , 3.5 percent  $\text{H}_2\text{O}$ , and 3.1 percent  $\text{Al}_2\text{O}_3$ , 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  $\text{CrOOH}$  (guyanaite) on heating were verified experimentally using a merumite

TABLE 6.—Analyses<sup>1</sup> of guyanaite from Guyana and Finland

| Constituent                       | Guyana (microchemical analysis) <sup>2</sup>   |  |       | Finland (mean of seven electron-probe analyses) <sup>3</sup>   |  |       |
|-----------------------------------|--|--|-------|--|--|-------|
|                                   | Percent of sample  | Equivalent $\text{H}_2\text{O}$ in $\text{R}_2\text{O}_3 \cdot \text{H}_2\text{O}$ | Ratio | Percent of sample  | Equivalent $\text{H}_2\text{O}$ in $\text{R}_2\text{O}_3 \cdot \text{H}_2\text{O}$ | Ratio |
| $\text{Cr}_2\text{O}_3$           | 4 71.7   | 12.9   | 0.472 | 75.76  | 13.64  | 0.492 |
| $\text{Al}_2\text{O}_3$           | 5 4.0  | .7   | .039  | 1.03   | .18  | .010  |
| $\text{Fe}_2\text{O}_3$           | 6 4.4  | .5   | .028  | 1.47   | .16  | .009  |
| $\text{V}_2\text{O}_5$            |  |  |       | 6.78   | .82  | .045  |
| $\text{Ti}_2\text{O}_3$           | 7 .86  | .1   | .006  |  |  |       |
| $\text{Mn}_2\text{O}_3$           | 8 .98  | .1   | .006  |  |  |       |
| $\text{H}_2\text{O}^+$            | 9 (8.7)  |  |       |  |  |       |
| $\text{H}_2\text{O}^-$            | 0  |  |       |  |  |       |
| $\text{H}_2\text{O}$ (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   |  |       |
|                                   | $(\text{Cr}_{1.78}\text{Al}_{0.08}\text{Fe}_{0.10}\text{Ti}_{0.02}\text{O}_3 \cdot \text{H}_2\text{O}$ |  |       | $\text{Mn}_{0.02}) (\text{Cr}_{1.77}\text{Al}_{0.04}\text{Fe}_{0.03}\text{V}_{0.16})_2\text{O}_3 \cdot \text{H}_2\text{O}$ |  |       |

<sup>1</sup> Spectrographic analysis of another (massive) sample containing eskolaite gave as minor constituents  $\text{As}_2\text{O}_3$ , 0.26 percent;  $\text{V}_2\text{O}_5$ , 0.22 percent;  $\text{Sb}_2\text{O}_3$ , 0.24 percent;  $\text{CaO}$ , 0.14 percent; and  $\text{Au}$ ,  $\text{Cu}$ ,  $\text{Mo}$ ,  $\text{Nb}$ ,  $\text{Pb}$ , and  $\text{Mg}$ , all 0.0x percent.

<sup>2</sup> Analyst, Blanche Ingram, U.S. Geological Survey. Approximately 25 mg of sample was fused with a mixture of  $\text{K}_2\text{CO}_3$  and  $\text{KClO}_4$ . The melt was leached with  $\text{H}_2\text{O}$  which separated  $\text{Fe}$ ,  $\text{Ti}$ , and  $\text{Mn}$  which remained in the residue, from  $\text{Cr}$  and  $\text{Al}$  which went into solution. Tests showed this separation reliable for the amount of  $\text{Al}$  present.  $\text{Cr}$  was determined on an aliquot of the water solution by titration with standard ferrous ammonium sulfate.

<sup>3</sup> Vuorelainen and others (1968)

<sup>4</sup> 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.

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

<sup>6</sup> The residue from the water leach of the fusion melt was dissolved in  $\text{HClO}_4$ , and the iron was determined colorimetrically on an aliquot using 1, 10-phenanthroline.

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

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

<sup>9</sup> A 12 mg sample was dried at  $110^\circ\text{C}$ . There was no measurable loss at  $110^\circ\text{C}$ . 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 CrO<sub>2</sub> 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 CrO<sub>2</sub>. 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 CrO<sub>2</sub>.

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 CrO<sub>2</sub> (rutile type) and observe that, "The introduction of H atoms into the rutile CrO<sub>2</sub> structure allows the formation of hydrogen bonds between the CrO<sub>6</sub> 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  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> is much more compact ( $G=5.21$  g cm<sup>-3</sup> vs. 4.0 g cm<sup>-3</sup> for CrO<sub>2</sub>) so that hydrogen atoms are not able to force an entry into the lattice and therefore Cr<sub>2</sub>O<sub>3</sub> 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)<sub>2</sub>O<sub>3</sub> from guyanaite, and CrO<sub>2</sub> from CrOOH

| (Cr, Al, Fe, Ti, Mn) O <sub>3</sub><br>(from guyanaite of film<br>00188 heated to 335°C)<br>(film 00189) |                       | CrO <sub>2</sub> (ignited CrOOH) <sup>1</sup><br>(Thamer and others, 1957) |                 |                |            |
|--|-----------------------|--|-----------------|----------------|------------|
| <i>I</i> <sup>2</sup>  | <i>d</i> <sup>2</sup> | <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        |

<sup>1</sup>  $a=4.421$ A,  $c=2.916$ A.

<sup>2</sup> 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)<sub>2</sub>O<sub>3</sub>

| (Cr, Al, Fe, Ti, Mn) <sub>2</sub> O <sub>3</sub> synthetic<br>(from guyanaite of film 00188<br>heated to 1,020°C) (film 00194) |          | Cr <sub>2</sub> O <sub>3</sub> (eskolaite), Finland<br>Kouvo and Vuorelainen, 1958) |          |
|--|----------|---|----------|
| <i>I</i> <sup>1</sup>  | <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    | -----   | -----    |

<sup>1</sup> 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<br>Pure brown crystals <sup>1</sup> |                |                 | Guyana<br>Greenish-black massive <sup>2</sup> |                       | Guyana<br>"Merumite"<br>(no. 238,<br>Berry and<br>Thompson,<br>1962) |          | Finland<br>Vuorelainen and others,<br>1968 |          |                | Tombs and<br>others, 1964 <sup>3</sup> |                       | Christensen, 1966 |                 |                 |            |
| <i>I</i> <sup>4</sup>                      | <i>d</i> (obs) | <i>d</i> (calc) | <i>hkl</i>                                    | <i>I</i> <sup>4</sup> | <i>d</i>   | <i>I</i> | <i>d</i>                                   | <i>I</i> | <i>d</i> (obs) | <i>d</i> (calc)                        | <i>I</i> <sup>4</sup> | <i>d</i> (obs)    | <i>I</i> (calc) | <i>d</i> (calc) | <i>hkl</i> |
|  |                |                 |   | vvw                   | <sup>5</sup> 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                    | <sup>5</sup> 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                    | <sup>5</sup> 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        |

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

<sup>2</sup> X-ray film 16821.

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

<sup>4</sup> 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.

<sup>5</sup> 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  $\alpha$ -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 eskolaite<sup>1</sup>  
[Analyst, J. I. Dinnin, U.S. Geological Survey]

| Constituent                                    | Percent | Equivalent H <sub>2</sub> O<br>(assuming<br>R <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O) |
|--|---------|--|
| Cr <sub>2</sub> O <sub>3</sub> <sup>2</sup>    | 70.6    | 8.36   |
| Fe <sub>2</sub> O <sub>3</sub> <sup>3</sup>    | 15.1    | 1.70   |
| Al <sub>2</sub> O <sub>3</sub>                 | 6.2     | 1.29   |
| Ti <sub>2</sub> O <sub>3</sub>                 | .17     | .02  |
| V <sub>2</sub> O <sub>3</sub>                  | .64     | .08  |
| H <sub>2</sub> O <sup>4</sup>                  | 6.9     |  |
| Total  | 99.6    | 3.09   |
| Ignition loss in argon (at 900°C) <sup>4</sup> |         | 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   |

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

<sup>2</sup> Chromium: A sample was decomposed by digestion with fuming per chloric 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.

<sup>3</sup> 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.

<sup>4</sup> H<sub>2</sub>O 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 Anhydrone 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 <sup>1</sup>   |
|------------------------------|--|
| 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. |

<sup>1</sup> 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 H<sub>2</sub>O is combined with Cr<sub>2</sub>O<sub>3</sub>, giving Cr<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O and (Cr,Fe,Al,Ti,V)<sub>2</sub>O<sub>3</sub>. The second method would be to assume that all of the H<sub>2</sub>O is combined with all of the minor oxides, plus some Cr<sub>2</sub>O<sub>3</sub>; this gives (Cr,Fe,Al,Ti,V)<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O + Cr<sub>2</sub>O<sub>3</sub>. The two computations follow:

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

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

In the computation of analysis to give density for case 1, where the analyzed sample is computed as 69.9 percent Cr<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O plus 30.2 percent (Cr<sub>0.25</sub>Fe<sub>0.44</sub>Al<sub>0.29</sub>Ti<sub>0.00</sub>V<sub>0.02</sub>)<sub>2</sub>O<sub>3</sub>, we have

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

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

and the computed density of the eskolaite in this sample is 4.86 gcm<sup>-3</sup>. The G<sub>CrOOH</sub> computes to 4.31 gcm<sup>-3</sup>. These values give a computed density of 4.480 gcm<sup>-3</sup> 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<sub>0.61</sub>Fe<sub>0.23</sub>Al<sub>0.15</sub>Ti<sub>0.00</sub>V<sub>0.01</sub>)<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O plus 32.7 Cr<sub>2</sub>O<sub>3</sub>, 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  $4.18 \text{ gcm}^{-3}$ . These values give a computed density of  $4.52 \text{ gcm}^{-3}$  for the analyzed sample as compared with a measured  $4.465 \pm 0.045$ .

These two sets of values may be averaged thus:

| Eskolaite  |                           |
|--|---------------------------|
| Compositon   | Density $\text{gcm}^{-3}$ |
| $(\text{Cr}_{0.25}\text{Fe}_{0.44}\text{Al}_{0.29}\text{Ti}_{0.00}\text{V}_{0.02})_2\text{O}_3$                              | 4.86                      |
| $\text{Cr}_2\text{O}_3$  | 5.21                      |
| $(\text{Cr}_{0.625}\text{Fe}_{0.22}\text{Al}_{0.145}\text{Ti}_{0.00}\text{V}_{0.01})_2\text{O}_3$                            | $5.035 \pm 0.175$         |
| Bracewellite   |                           |
| Compositon   | Density $\text{gcm}^{-3}$ |
| $\text{CrOOH}$   | 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)             |
| $(\text{Cr}_{0.805}\text{Fe}_{0.115}\text{Al}_{0.075}\text{Ti}_{0.00}\text{V}_{0.005})_2\text{O}_3 \cdot \text{H}_2\text{O}$ | $4.24 \pm 0.065$          |

Finally, these averaged values give computed densities of  $4.48 \text{ gcm}^{-3}$  (case 1) and  $4.50 \text{ gcm}^{-3}$  (case 2) for the analyzed sample as compared with the measured  $4.465 \pm 0.045$ , 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  $4.86 \text{ gcm}^{-3}$  the computed density of the analyzed sample is  $4.46 \text{ gcm}^{-3}$  as compared with the measured  $4.465 \pm 0.045$ .

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

and as

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

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

Then,

|  | From published data | From analysis | From X-ray    |
|--|---------------------|---------------|---------------|
| $(\text{Cr}_{0.25}\text{Fe}_{0.44}\text{Al}_{0.29}\text{Ti}_{0.00}\text{V}_{0.02})_2\text{O}_3$ (eskolaite)                  | ---                 | 4.86          | ---           |
| $\text{Cr}_2\text{O}_3$  | 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) |
| $\text{CrOOH}$ (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  $\text{CrOOH}$ .

#### 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  $\mu$  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  $\text{Fe}_2\text{O}_3$ ) and, to a lesser degree, in alumina (2–5 percent  $\text{Al}_2\text{O}_3$ ).

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

["Spec" pure  $\text{Cr}_2\text{O}_3$ , analyzed  $\text{FeS}_2$ , and  $\text{Al}_2\text{O}_3$  were used as reference standards.  $\text{CrK}\alpha$  and  $\text{FeK}\alpha$  were measured using the LiF analyzing crystal;  $\text{AlK}\alpha$  was measured using potassium acid phthalate. All analyses were performed at 20 kv with a specimen current of 0.01  $\mu\text{amp}$ . Analyst, E. J. Dwornik, U.S. Geological Survey]

| Crystal      | $\text{Al}_2\text{O}_3$ | $\text{Fe}_2\text{O}_3$ | $\text{Cr}_2\text{O}_3$ | Equivalent $\text{H}_2\text{O}$ | 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 <sup>2</sup> | Bracewellite (massive)<br>(X-ray film 16775) |          | hkl | Merumite (massive<br>bracewellite + eskolaite) <sup>1</sup><br>(X-ray film 16761) |                      | Bracewellite (red<br>pure crystals)<br>(X-ray film 16763) |                      | Goethite<br>(Brown, 1961) |         | Eskolaite<br>(Guyana)<br>(X-ray film 16765) |                |         |
|----------------|--|----------|-----|---|----------------------|---|----------------------|---------------------------|---------|---|----------------|---------|
|                | d (obs)                                      | d (calc) |     | I <sup>2</sup>  | d (obs)              | I <sup>2</sup>  | d (obs)              | I                         | d (obs) | hkl   | I <sup>2</sup> | 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   | <sup>2</sup> E 3.604 | vw  | <sup>2</sup> E 3.604 |                           |         |   | vs             | 3.601   |
| vw             | 3.319  | 3.320    | 120 |   |                      |   |                      | 10                        | 3.38    | 120   |                |         |
|                |  |          |     |   |                      | vw  | 3.314                |                           |         |   |                |         |
| w              | <sup>2</sup> G 3.236                         |          |     | w   | <sup>2</sup> 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   |                |         |

<sup>1</sup> See table 10 for analysis.

<sup>2</sup> 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  $2.0 \pm 0.1$  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  $4.12 \text{ gm}^{-3}$  (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  $5.49 \text{ gm}^{-3}$  (calculated,  $5.609 \text{ gm}^{-3}$ ) of Dannhauser and Vaughan (1955). Stroupe (1949) gave a "rough" density of  $7.0 \text{ gm}^{-3}$ .

Accordingly, for the natural complex grimaldiite-mcconnellite crystals, observed refractive indices should range from  $\epsilon$  of CrOOH (1.975) to the  $\omega$  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  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  as substitutions for  $\text{Cr}_2\text{O}_3$  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  $\text{Cu}_2\text{O}$ , 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  $350^\circ\text{C}$  to a mixture of  $\text{CrO}_2$  and  $\text{Cr}_2\text{O}_3$ . 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 analysis<sup>1</sup> 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) $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$ |         | $\text{Cr}_2\text{O}_3 \cdot \text{Cu}_2\text{O}$ |         | $\text{Cr}_2\text{O}_3 \cdot \text{H}_2\text{O}$ |         | $\text{H}_2\text{O}$ |         |
|-------------------------------|-------------|----------------------------------|------------|---|---------|---|---------|--|---------|----------------------|---------|
|                               |             |                                  |            | Mole ratio  | Percent | Mole ratio  | Percent | Mole ratio                                       | Percent | Mole ratio           | Percent |
| $\text{Cr}_2\text{O}_3$ ----- | 77.3        | 77.3                             | 509        | -----   | -----   | 35  | 5.3     | 474  | 72.0    | -----                | -----   |
| CuO -----                     | 5.5         | ( $\text{Cu}_2\text{O}$ ) 4.95   | 35         | -----   | -----   | 35  | 4.95    | -----  | -----   | -----                | -----   |
| $\text{Al}_2\text{O}_3$ ----- | 4.3         | 4.3                              | 42         | 42  | 4.3     | -----   | -----   | -----  | -----   | -----                | -----   |
| $\text{Fe}_2\text{O}_3$ ----- | .85         | .85                              | 5          | 5   | .85     | -----   | -----   | -----  | -----   | -----                | -----   |
| SiO -----                     | .42         | -----                            | -----      | -----   | -----   | -----   | -----   | -----  | -----   | -----                | -----   |
| $\text{H}_2\text{O}$ -----    | .00         | .00                              | -----      | -----   | -----   | -----   | -----   | -----  | -----   | -----                | -----   |
| Ignition loss -----           | 11.5        | ( $\text{H}_2\text{O}^+$ ) 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                  | -----   |

<sup>1</sup> 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  $\text{H}_2\text{O}^-$  and loss on ignition by gravimetry.

Copper is recomputed as  $\text{Cu}_2\text{O}$ , rather than the CuO reported by the analyst. On ignition, the  $\text{Cu}_2\text{O}$  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  $\text{CrO}_2$  at  $350^\circ\text{C}$ , rhombohedral CrOOH at this temperature changes slowly and partially to a mixture of  $\text{CrO}$ , and  $\text{Cr}_2\text{O}_3$ ; when the rhombohedral CrOOH is completely changed, there is no reduction of  $\text{CrO}_2$  to  $\text{Cr}_2\text{O}_3$ .

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 |
| $\text{H}_2\text{O}$ (excess) ----- | 2.7 - 2.7   |
| Total -----                         | 99.45-99.45 |

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

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

<sup>1</sup> Sample (1 mg) is different from that in table 12.

<sup>2</sup> See footnote on reliability of determinations, table 2, footnote 4.

<sup>3</sup> 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 CrO<sub>2</sub> complex forms layers which are then connected by the cations—in this case H<sup>+</sup> and Cu<sup>+</sup>. Interlayer substitution in this respect should take place easily, but the large difference in atomic diameters of H<sup>+</sup> and Cu<sup>+</sup> 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 16.—X-ray powder pattern of grimaldiite and mcconnellite

| Grimaldiite-<br>mcconnellite <sup>1</sup><br>(+ quartz)<br>X-ray film 16794 | HCrO <sub>2</sub><br>XPDF 9-331<br>(Thamer and others 1957) |         |      |         |                       | "α-CrOOH"<br>(Torokin and<br>others, 1968) |      | Cu <sub>2</sub> O·Cr <sub>2</sub> O <sub>3</sub><br>XPDF 5-668<br>(Stroupe, 1949) |     |         | Mcconnellite<br>(film 16794) |                  |         |                       |
|---|---|---------|------|---------|-----------------------|--|------|---|-----|---------|------------------------------|------------------|---------|-----------------------|
|   | I <sup>2</sup>  | d (obs) | I    | d (obs) | d (calc) <sup>3</sup> | hkl <sup>3</sup>                           | I    | d (obs)   | I   | d (obs) | d (calc) <sup>4</sup>        | hkl <sup>4</sup> | d (obs) | d (calc) <sup>5</sup> |
| vw  | 10.05   |         |      |         |                       |  |      |   |     |         |                              |                  |         |                       |
| vw  | 4.97  |         |      |         |                       |  |      |   |     |         |                              |                  |         |                       |
| vvs   | 4.47  | 100     | 4.44 | 4.47    | 003                   | 3  | 4.46 |   |     |         |                              |                  |         |                       |
| w   | 3.33  | Q       |      |         |                       |  |      |   |     |         |                              |                  |         |                       |
| vw  | 3.22  |         |      |         |                       |  |      |   |     |         |                              |                  |         |                       |
| ms  | 2.85  | M       |      |         |                       |  |      |   |     |         |                              |                  |         |                       |
|   |   |         |      |         |                       |  |      |   | 40  | 2.85    | 2.850                        | 006              | 2.85    | 2.860                 |
|   |   |         |      |         |                       |  |      |   | 20  | 2.570   | 2.547                        | 101              |         | 2.555                 |
| w   | 2.528   |         | 5    | 2.529   | 2.537                 | 101  | 9    | 2.51  |     |         |                              |                  |         |                       |
| ms  | 2.462   | M       |      |         |                       |  |      |   | 100 | 2.470   | 2.467                        | 012              | 2.462   | 2.474                 |
| vs  | 2.401   |         | 30   | 2.407   | 2.411                 | 012  |      |   |     |         |                              |                  |         |                       |
| vw  | 2.232   |         | 5    | 2.227   | 2.233                 | 006  |      |   |     |         |                              |                  |         |                       |
| vw  | 2.21  | M       |      |         |                       |  |      |   | 40  | 2.210   | 2.207                        | 104              | 2.21    | 2.213                 |
| vw  | 2.040   |         | 5    | 2.042   | 2.046                 | 104  |      |   |     |         |                              |                  |         |                       |
| vvw   | 1.99  |         |      |         |                       |  |      |   |     |         |                              |                  |         |                       |
|   |   |         |      |         |                       |  |      |   | 5   | 1.911   | 1.900                        | 009              |         | 1.907                 |
| vs  | 1.857   |         | 25   | 1.858   | 1.860                 | 015  | 2    | 1.861   |     |         |                              |                  |         |                       |
|   |   |         |      |         |                       |  |      |   | 45  | 1.646   | 1.645                        | 018              | 1.64    | 1.650                 |
| mw  | 1.537   |         | 10   | 1.536   | 1.538                 | 107  |      |   |     |         |                              |                  |         | 1.4915                |
|   |   |         |      |         |                       |  |      |   |     |         |                              |                  |         |                       |
|   |   |         |      |         |                       |  |      |   |     |         |                              |                  |         |                       |
| ms  | 1.486   |         | 15   | 1.490   | 1.489                 | 009  | 10   | 1.489   | 35  | 1.488   | 1.487                        | 110              |         | 1.4915                |
|   |   |         |      |         |                       |  |      |   | 5   | 1.439   | 1.493                        | 113              |         | 1.443                 |
| vw  | 1.420   | M       |      |         |                       |  |      |   | 30  | 1.426   | 1.425                        | 0012             | 1.420   | 1.430                 |
| w   | 1.409   |         | 10   | 1.414   | 1.415                 | 113  | 2    | 1.414   |     |         |                              |                  |         | 1.429                 |
|   |   |         | 5    | 1.404   | 1.406                 | 018  |      |   |     |         |                              |                  |         |                       |
|   |   |         |      |         |                       |  |      |   | 20  | 1.319   | 1.319                        | 116              |         | 1.322                 |
|   |   |         |      |         |                       |  |      |   | 15  | 1.275   | 1.274                        | 202              |         | 1.277                 |
| w   | 1.267   |         | 5    | 1.266   | 1.269                 | 202  | 2    | 1.263   |     |         |                              |                  |         |                       |
|   |   |         |      |         |                       |  |      |   |     |         |                              |                  |         |                       |
|   |   |         |      |         |                       |  |      |   |     |         |                              |                  |         |                       |

<sup>1</sup> Unit-cell refinements (table 17) of the two phases have been successfully carried out using Evans and others (1963) program.

<sup>2</sup> vvs, very very strong; vs, very strong; ms, medium strong; w, weak; mw, medium weak; vw, very weak; vvw, very very weak; Q strongest quartz line; M, mcconnellite lines.

<sup>3</sup> Computed on hexagonal cell having  $a=2.984\text{Å}$ ,  $c=13.40\text{Å}$  by Thamer and others (1957) who give slightly different  $d(\text{calc})$ .

<sup>4</sup> Computed from  $a=2.9747\pm 0.00014\text{Å}$ ,  $c=17.1015\pm 0.0005\text{Å}$ .

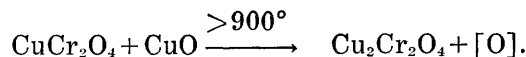
<sup>5</sup> Computed from X-ray powder film 16794 (above, first column) using  $a$  and  $c$  of Dannhauser and Vaughan (1955) (see table 17) as initial parameters for the least squares analysis.

1957) studied the infrared absorption spectrum, finding that it had no resemblance to that of diaspore, AlOOH.

Torokin and others (1968) have also formed grimaldiite by heating (synthetic)  $\gamma$ -CrOOH to 340°–360°C at 300–350 atm pressure for 2 hr. With little change in water content (from 1.54 to 1.51 moles per mole Cr<sub>2</sub>O<sub>3</sub>) the color changes from emerald green to dirty violet, and the X-ray powder pattern changes from that given in table 18 to that ( $\alpha$ -CrOOH) given in table 16. Grimaldiite was also formed directly by heating an ammoniacal chromium nitrate solution at 320°C and 200 atm for 2 hr.

Gröger (1912) appears to have been the first to synthesize rhombohedral CrOOCu by heating basic cupric chromite (CuCr<sub>2</sub>O<sub>4</sub>) for 6 hr at 1,000°C. Stroupe (1949) synthesized the compound in two other ways: first, by igniting cupric chromite

2 CuCr<sub>2</sub>O<sub>4</sub>  $\xrightarrow{>900^\circ}$  Cu<sub>2</sub>Cr<sub>2</sub>O<sub>4</sub> (that is CrOOCu) + Cr<sub>2</sub>O<sub>3</sub> + [O];  
second, by heating equimolar cupric chromite and cupric oxide:



Stroupe repeated Gröger's synthesis but did not obtain usable single crystals; those he did obtain by his own methods afforded good single-crystal X-ray data as well as characteristic powder patterns (table 16).

Dannhauser and Vaughan (1955) determined the structure of CrOOCu and indicated its relation to delafossite FeOOCu. They reported that CrOOCu ("cuprous chromite") is rhombohedral, with apparent hexagonal symmetry arising from extensive twinning, the twins being related by 60° rotation about the hexagonal  $c$  axis. Their cell constants are comparable with data for the isostructural CrOOH (table 17). These data are for the mcconnellite hexagonal lattice; for the primitive rhombohedral cell, the parameters are  $a=5.9536\pm 0.0002\text{Å}$ ,  $\alpha=28^\circ 56.0' \pm 0.1'$ .

#### RELATION OF MCCONNELLITE TO DELAFOSSITE

The structural relationship of mcconnellite, CrOOCu, to delafossite, FeOOCu, indicated by Dannhauser and Vaughan (1955) appears to be

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

|   | $a$<br>(angstroms) | $c$<br>(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<br>(stainierite)<br>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<br>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<br>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  $\text{CuFeO}_2$  and copper ferrite  $\text{CuFe}_2\text{O}_4$  (a spinel) were the only ternary phases. Similarly, Wiedersich and others (1968) showed that from initial mixtures of

$\text{Cu}_2\text{O}$  or  $\text{CuO}$  and  $\text{Fe}_2\text{O}_3$ , or of  $\text{Cu}_2\text{O}$  and  $\text{FeO}$  or  $\text{Fe}_3\text{O}_4$ , only  $\text{CuFeO}_2$  (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 ( $\text{CrOOCu}$ ) as valid.

Mcconnellite,  $\text{CrOOCu}$ , is therefore, as suggested by Dannhauser and Vaughan (1955), isostructural with delafossite,  $\text{FeOOCu}$ . Hey (1968) has analyzed natural delafossite from Nizhnii Tagil, U.S.S.R. (the type locality) and Kimberly, Nevada, confirming the accepted formula  $\text{FeOOCu}$ . 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  $\text{CoOOH}$  (heterogenite),  $\text{MnOOH}$  (feitknechtite), and  $\text{NiOOH}$  (synthetic), and with  $\text{NaHF}_2$  and  $\text{CsICl}_2$  (table 24).

#### $\gamma$ -CrOOH (SYNTHETIC)

Besides the three new natural polymorphs of  $\text{CrOOH}$  found in merumite, a fourth is known only as a synthetic product. It is termed  $\gamma$ -CrOOH and is very probably isostructural with the common orthorhombic dipyramidal minerals boehmite ( $\gamma$ - $\text{AlOOH}$ ), lepidocrocite ( $\gamma$ - $\text{FeOOH}$ ), and synthetic  $\gamma$ - $\text{ScOOH}$ , whose cell constants are all given in table 19. Alario Franco and Sing (1972) refer to " $\gamma$ -CrOOH" as "similar to boehmite." However, no single-crystal work has been done on  $\gamma$ -CrOOH; Christensen (written commun., 1971) notes that " $\gamma$ -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  $\gamma$ -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  $\gamma$  forms of  $\text{AlOOH}$ ,  $\text{CrOOH}$ , and  $\text{FeOOH}$ , further showing the isotropy.

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  $\text{H}_2\text{O}$  per one mole of  $\text{Cr}_2\text{O}_3$ . 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  $\gamma$ -CrOOH to  $\alpha$ -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  $\gamma$ -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  $\gamma$ -CrOOH and lepidocrocite

| $\gamma$ -CrOOH (Torokin and others, 1968) |       |                         |        | Lepidocrocite (Rooksby, 1951) |       |          |
|--|-------|-------------------------|--------|-------------------------------|-------|----------|
| $l$  | $d$   | $d$ (calc) <sup>1</sup> | $hkl$  | $l$                           | $d$   | $hkl$    |
| 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 |          |

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

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

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

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

ELECTRON-PROBE ANALYSIS

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  $\mu$ amp.

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

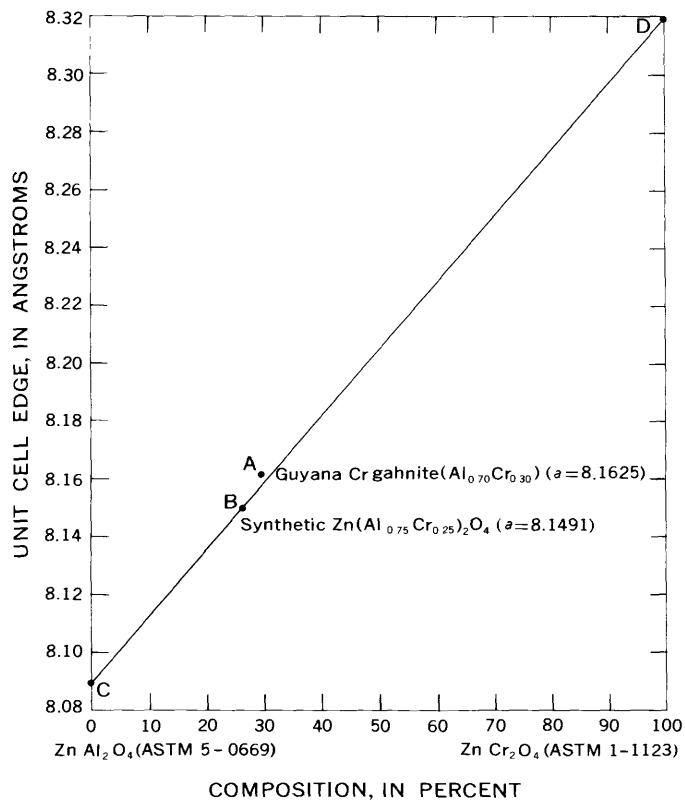


FIGURE 4.—Graph of unit cell edge versus composition in natural and synthetic chromian gahnite. A, Composition of chromian gahnite from Guyana was computed from cubic cell constant. B, Cubic cell constant of synthetic chromian gahnite was computed from X-ray powder pattern. C, Composition and cubic cell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

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> <sup>5</sup>           | <i>d</i> (obs) | <i>d</i> (calc)                   | <i>l</i> <sup>5</sup> | <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                              |                       |               | 1        | 733        |
|               |          | vw                              | .944           | .942                              |                       |               | 5        | 822        |
|               |          |                                 |                |                                   |                       |               | 9        | 751        |

Plus additional weak lines.

<sup>1</sup> Synthetic zinc chromite,  $ZnCr_2O_4$ , prepared by New Jersey Zinc Co., XPDF card 1-1122.  $a=8.32A$ .

<sup>2</sup> Chromian gahnite,  $Zn(Al_{0.7}, Cr_{0.3})_2O_4$ , from Guyana.  $a=8.1625A$ .

<sup>3</sup> Synthetic compound,  $Zn(Al_{0.75}, Cr_{0.25})_2O_4$ , prepared by Jun Ito, Harvard University (written commun., 1968).  $a=8.1491A$ .

<sup>4</sup> Synthetic zinc aluminate (gahnite),  $ZnAl_2O_4$ , prepared by RCA Laboratory, XPDF 5-0669.  $a=8.0848A$ .

<sup>5</sup> 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  $\text{Cr}_2\text{O}_3$  respectively; therefore, about a tenth of  $\text{Al}_2\text{O}_3$  is replaced by  $\text{Cr}_2\text{O}_3$ .

Chromian pyrophyllite has also been reported from Salzburg, Austria (Meixner, 1961), with about 1 percent Cr ( $\cong 2.93$  percent  $\text{Cr}_2\text{O}_3$ ). 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 <sup>1</sup>                                | Au   | Ag  |
|--|--|---|
| A----60 ppm (2 oz/ton) <sup>2</sup>                | 0.03 percent (10 oz/ton) <sup>4</sup>        | 3 ppm <sup>3</sup><br>0.003 percent <sup>4</sup>  |
| B----4 ppm <sup>2</sup>                            | Not detected <sup>4</sup>                    | <1 ppm <sup>3</sup><br>Not detected. <sup>4</sup> |
| C----2 ppm <sup>2</sup>                            | Not detected <sup>4</sup>                    | <1 ppm <sup>3</sup><br>Not detected. <sup>4</sup> |
| D----0.5 ppm <sup>2</sup>                          | Not detected <sup>4</sup>                    | <1 ppm <sup>3</sup><br>Not detected. <sup>4</sup> |
| E----Looked for but<br>Not detected <sup>2</sup> . | 0.7 ppm <sup>6</sup><br>0.9 ppm <sup>7</sup> | 0.00002 percent <sup>5</sup> (0.2 ppm)            |
| F----0.07 percent (23 oz/ton) <sup>8</sup>         |  | 0.0017 percent <sup>8</sup> (10 ppm)              |

<sup>1</sup> 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.

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

<sup>3</sup> $\text{HNO}_3$  boil-atomic absorption method; 1-gram samples; analysts, J. D. Mensik and J. A. Thomas.

<sup>4</sup>Spectrographic 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."

<sup>5</sup>Spectrographic method, as above; analyst, Helen W. Worthing.

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

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

Gold determined fluorimetrically as the Rhodamine B Chloraurate.

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



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

| X-ray film 678<br>Guyana <sup>1</sup> |          | X-ray film 687<br>Guyana <sup>2</sup> |          | Average of topaz from Brazil,<br>Mexico, and Utah <sup>3</sup><br>XPDF 12-765 |          |            |
|---------------------------------------|----------|---------------------------------------|----------|---|----------|------------|
| <i>l</i> <sup>4</sup>                 | <i>d</i> | <i>l</i> <sup>4</sup>                 | <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    |                                       |          |   |          |            |

<sup>1</sup> Light flesh-colored rounded grains of topaz, Director Creek, Guyana.

<sup>2</sup> Reddish-brown topaz, Director Creek, Guyana.

<sup>3</sup> Swanson and others (1962).

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

<sup>1</sup> Blanche Ingram, U.S. Geological Survey, analyst; Claude Waring, U.S. Geological Survey, determined (spectrographically) Fe 0.03 percent, Mg 0.01 percent.

<sup>2</sup> Pardee, Glass, and Stevens, 1937.

<sup>3</sup> The sample (2 mg) was fused with NaOH, and the solution from the fusion was used to determine Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> spectrophotometrically. Al<sub>2</sub>O<sub>3</sub> was determined with alizarin red S and SiO<sub>2</sub> as the molybdenum blue complex. The amount of F in the aliquot used for measurement of Al<sub>2</sub>O<sub>3</sub> was below the interference level.

<sup>4</sup> The sample (approximately 25 mg) was fused with Na<sub>2</sub>CO<sub>3</sub> and dissolved in perchloric acid; Ti was determined spectrophotometrically with Tiron.

<sup>5</sup> The sample (100 mg) was heated at 110°C to constant weight to determine —H<sub>2</sub>O. The sample was then mixed with twice its weight of freshly fused sodium tungstate, and +H<sub>2</sub>O 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. H<sub>2</sub>O and CO<sub>2</sub> were absorbed and weighed.

<sup>6</sup> F was determined by a specific ion-electrode procedure. Samples of 10 mg each were decomposed by fusing with Na<sub>2</sub>CO<sub>3</sub>-ZnO, and the F was leached with H<sub>2</sub>O. Measurement of F was made in a 0.5 M sodium citrate solution to prevent Al interference.

<sup>7</sup> 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 H<sub>2</sub>O (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-

TABLE 24.—Crystallographic relationship of the CrOOH compounds and other metallic hydroxides (values in angstroms)

|                                | Pnmm  |       |       | Orthorhombic |        |       | Amam                       |       |       | Rhombohedral |                            |      |       |
|--------------------------------|-------|-------|-------|--------------|--------|-------|----------------------------|-------|-------|--------------|----------------------------|------|-------|
|                                | a     | b     | c     | a            | b      | c     | a                          | b     | c     | a            | b                          | c    |       |
| CrO(OH)                        |       |       |       |              |        |       |                            |       |       |              |                            |      |       |
| AlO(OH)                        |       |       |       |              |        |       |                            |       |       |              |                            |      |       |
| FeO(OH)                        |       |       |       |              |        |       |                            |       |       |              |                            |      |       |
| ScOOH <sup>8, 10</sup>         |       |       |       |              |        |       |                            |       |       |              |                            |      |       |
| InOOH <sup>4, 10</sup>         |       |       |       |              |        |       |                            |       |       |              |                            |      |       |
| CoO(OH)                        |       |       |       |              |        |       |                            |       |       |              |                            |      |       |
| NiOOH <sup>10</sup>            |       |       |       |              |        |       |                            |       |       |              |                            |      |       |
| MnO(OH)                        |       |       |       |              |        |       |                            |       |       |              |                            |      |       |
| (V,Fe)O(OH)                    |       |       |       |              |        |       |                            |       |       |              |                            |      |       |
| GaO(OH)                        |       |       |       |              |        |       |                            |       |       |              |                            |      |       |
| RhO(OH)                        |       |       |       |              |        |       |                            |       |       |              |                            |      |       |
| NaHF <sub>2</sub>              |       |       |       |              |        |       |                            |       |       |              |                            |      |       |
| CsCl <sub>2</sub>              |       |       |       |              |        |       |                            |       |       |              |                            |      |       |
| Guyanaite <sup>1, 2, 10</sup>  | 4.86  | 4.295 | 2.95  | 4.492        | 9.860  | 2.97  | α-CrOOH <sup>1</sup>       | 3.89  | 12.7  | 2.92         | Grimaldite <sup>1, 2</sup> | 2.99 | 13.40 |
| Bracewellite <sup>1, 2</sup>   |       |       |       | 4.41         | 9.40   | 2.84  | Boehmite <sup>2</sup>      | 3.69  | 12.2  | 2.86         |                            |      |       |
| Diaspore <sup>2</sup>          |       |       |       | 4.65         | 10.02  | 3.04  | Lepidocrocite <sup>2</sup> | 3.88  | 12.54 | 3.07         |                            |      |       |
| Goethite <sup>2</sup>          |       |       |       | 4.755        | 10.301 | 3.209 | α-ScOOH <sup>2, 3</sup>    | 4.01  | 13.01 | 3.24         |                            |      |       |
| α-ScOOH <sup>3</sup>           |       |       |       |              |        |       | CoOOH <sup>10</sup>        | 4.353 | 9.402 | 2.840        |                            |      |       |
| CoOOH <sup>10</sup>            |       |       |       | 4.31         | 13.90  | 2.925 | α-NiOOH <sup>11</sup>      | 4.40  | 13.8  | 2.82         |                            |      |       |
| α-NiOOH <sup>12</sup>          |       |       |       | 4.56         | 10.70  | 2.85  |                            |       |       |              |                            |      |       |
| Grouitite <sup>2</sup>         |       |       |       | 4.54         | 9.97   | 3.03  |                            |       |       |              |                            |      |       |
| Montroseite <sup>3</sup>       |       |       |       | 4.51         | 9.75   | 2.965 |                            |       |       |              |                            |      |       |
| GaOOH <sup>5</sup>             |       |       |       | 4.92         | 11.3   | 3.44  |                            |       |       |              |                            |      |       |
| LaOOH <sup>5</sup>             |       |       |       |              |        |       |                            |       |       |              |                            |      |       |
| RhOOH <sup>10</sup>            | 4.924 | 4.291 | 3.082 |              |        |       |                            |       |       |              |                            |      |       |
| NaHF <sub>2</sub> <sup>6</sup> |       |       |       |              |        |       |                            |       |       |              |                            |      |       |
| CsCl <sub>2</sub> <sup>7</sup> |       |       |       |              |        |       |                            |       |       |              |                            |      |       |

1. This report.
2. Strunz, 1970.
3. Christensen and Jensen, 1967.
4. Lehmann and others, 1970.
5. Yamaguchi and Katsurai, 1967.
6. Swanson and others, 1955.
7. Swanson and others, 1954.
8. Christensen, 1971.
9. Erd, K. C. U.S. Geological Survey, written commun., 1972.
10. Chenavas and others, 1973.
11. Bode, 1961.
12. Evans, Howard, U.S. Geological Survey, written commun., 1974.

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).

#### REFERENCES CITED

- Alario Franco, M. A., and Sing, K. S. W., 1972, The interconversion of orthorhombic chromium oxyhydroxide and chromium dioxide: *Jour. Thermal Analysis*, v. 4, p. 47-52.
- Auer-Welsbach, Helga, and Seifert, K., 1962, ScOOH: *Monatsh. Chemie*, v. 93, p. 1110-1113.
- Berry, L. G., and Thompson, R. M., 1962, X-ray powder data for ore minerals—The Peacock atlas: *Geol. Soc. America Mem.* 85, 281 p.
- Bode, Hans, 1961, Chemische Vorgänge auf Elektroden von galvanischen Stromquellen: *Angew. Chemie*, v. 73, p. 553-560.
- Bracewell, Smith, 1946, The geology and mineral resources of British Guiana, from *Handbook of natural resources of British Guiana: Georgetown, Demarara, British Guiana Interior Devel. Comm.*, 40 p.
- Brown, George, ed., 1961, The X-ray identification and crystal structures of clay minerals: *Mineralog. Soc. London*, p. 386.
- Buist, D. S., Gadalla, A. M. M., and White, J., 1966, Delafossite and the system Cu-Fe-O: *Mineralog. Mag.*, v. 35, p. 731-741.
- Chenavas, J., Joubert, J. C., Capponi, J. J. and Marezio, M. (1973) Synthèse de Nouvelles Phases Denses D'oxyhydroxydes  $M^{3+}$ OOH des Metaux de la Première Serie de Transition, en Milieu Hydrothermal a Tres Haute Pression: *Jour. Solid State Chem.* v. 6, p. 1-15.
- Christensen, A. N., 1966, The crystal structure of a new polymorph of CrOOH: *Inorganic Chemistry*, v. 5, no. 8, p. 1452-1453.
- 1971, Hydrothermal preparation of some oxides and some oxide hydroxides at temperatures up to 900°C and pressures up to 80 Kb: *Materials Research Bull.*, v. 6, no. 8, p. 691-698.
- Christensen, A. N., Grønbaek, R., and Rasmussen, S. E., 1964, The crystal structure of InOOH: *Acta Chemica Scandinavica*, v. 18, no. 5, p. 1261-1266.
- Christensen, A. N., and Jensen, S. J., 1967, Hydrothermal preparation of  $\alpha$ -ScOOH and of  $\gamma$ -ScOOH, Crystal Structure of  $\alpha$ -ScOOH: *Acta Chemica Scandinavica*, v. 21, p. 121-126.
- Croft, W. J., Tombs, N. C., and England, R. E., 1964, Crystallographic data for pure crystalline silver ferrite: *Acta Cryst.*, v. 17, p. 313.
- Dannhauser, Walter, and Vaughan, P. A., 1955, The crystal structure of cuprous chromite: *Am. Chem. Soc. Jour.*, v. 77, p. 896-897.
- Dixon, C. G., 1957, Merumite: *British Guiana Geol. Survey Dept. Mineral Resources Pamph.* no. 5, 9 p. and map (mimeographed).
- Donath, M., 1931, Zinc-bearing chromite: *Am. Mineralogist*, v. 16, p. 484-487.
- Douglass, R. M., 1957, The crystal structure of HCrO<sub>2</sub>: *Acta Cryst.*, v. 10, p. 423-427.
- Evans, H. T., Jr., Appleman, D. E., and Handwerker, D. S., 1963, The least squares refinement of crystal unit cells with powder diffraction data by an automatic computer indexing method [abs.]: *Am. Cryst. Assoc., Ann. Mtg.*, Cambridge, Mass., March 1963, Program and Abs., Abs. E-10, p. 42-43.
- Gessner, W., 1967, Über die Modifikationen der "Aluminate" Me'Al<sub>2</sub> des einwertigen Ag, Cu, und Tl: *Zeitschr. Anorg. u. Allg. Chemie* 352, p. 145-155.
- Gröger, M., 1912, Chromite aus basischen Chromaten: *Zeitschr. Anorg. u. Allg. Chemie*, v. 76, p. 30-38.
- Hahn, H., and de Lorent, C., 1955, Versuche zur Darstellung ternärer Oxyde des Aluminiums, Galliums, und Indiums mit einwertigen Kupfer und Silber: *Zeitschr. Anorg. u. Allg. Chemie*, v. 297, p. 281-288.
- Hey, M. H., 1968, On the composition of natural delafossite: *Mineralog. Mag.*, v. 36, p. 651-653.
- Hund, F., 1959, Struktur von  $\gamma$ -CrOOH: *Noturwissenschaften*, v. 36, p. 320-321.
- Kondrashev, Yu. D., and Federova, N. N., 1954, Crystal structure of CoH<sub>2</sub>O: *Acad. Sci. USSR Computes Rendu*, v. 94, p. 229-231.
- Kouvo, Olavi, and Vuorelainen, Yrjö, 1958, Eskolaite, a new chromium mineral: *Am. Mineralogist*, v. 43, p. 1098-1106.
- Laubengayer, A. W., and McCune, H. W., 1952, New crystalline phases in the system chromium (III) oxide-water: *Am. Chem. Soc. Jour.*, v. 74, p. 2362-2364.
- Lehmann, M. S., Larsen, F. K., Poulsen, F. R., Christensen, A. N., and Rasmussen, S. E., 1970, Neutron and X-ray crystallographic studies on indium oxide hydroxide: *Acta Chemica Scandinavica*, v. 24, p. 1662-1670.
- Meixner, Heinz, 1961, Chrom-pyrophyllit aus der Cu-Lagerstätte von Mühlbach/Hochkönig (Salzburg) und Betrachtungen zur Entstehung von Al-Silikaten bei der Vererzung und bei späterer Verwitterung in einigen Vorkommen der Ostalpen: *Chemie Erde*, v. 21, p. 1-4.
- Milligan, W. O., and McAtee, J. L., 1956, Structure of  $\gamma$ -AlOOH and ScOOH: *Jour. Phys. Chem.*, v. 60, p. 273-277.
- Milton, Charles, Appleman, Daniel, Chao, E. C. T., Cuttitta, Frank, Dinnin, J. I., Dwornik, E. J., Hall, M., Ingram, B. L., and Rose, H. J., Jr., 1968, Mineralogy of merumite, a unique assemblage of chromium minerals from Guyana [abs.]: *Geol. Soc. America Spec. Paper* 115, p. 151-152.

- Milton, Charles, and Chao, E. C. T., 1958, Eskolaite,  $\text{Cr}_2\text{O}_3$ , in "merumite" from British Guiana: *Am. Mineralogist*, v. 43, p. 1203.
- Milton, Charles, and Narain, Sat, 1969, Merumite occurrence in Guyana: *Econ. Geology*, v. 64, p. 910-914.
- Pabst, A., 1938, Crystal structure and density of delafossite [abs.]: *Am. Mineralogist*, v. 23, p. 175-176.
- Pardee, J. T., Glass, J. J., and Stevens, R. E., 1937, Massive low-fluorine topaz from Brewer mine, South Carolina: *Am. Mineralogist*, v. 22, p. 1058-1064.
- Pearre, N. C., and Heyl, A. V., Jr., 1960, Chromite and other mineral deposits in serpentine rocks of the Piedmont Upland, Maryland, Pennsylvania, and Delaware: *U.S. Geol. Survey Bull.* 1082-K, p. 707-833.
- Ramdohr, Paul, 1960, *Die Erzminerale und ihre Verwachsungen*: 3d ed., Berlin, Akad.-Verlag, 1089 p.
- 1969, *The ore minerals and their intergrowths*. Oxford-New York. Pergamon Press, 1174 p.
- Reichert, P. P., and Yost, W. J., 1946, The crystal structure of synthetic boehmite: *Jour. Chem. Physics*, v. 14, p. 495-501.
- Rooksby, H. P., 1951, in Brindley, G. W., ed., *X-ray identification and crystal structures of clay minerals*. London Mineralog. Soc. (Clay Minerals Group), p. 264.
- Seeliger, E., and Mücke, A., 1969, Donathite, ein tetragonaler Zn-reicher Mischkristall von Magnetit und Chromit: *Neues Jahrb. Mineralogie Monatsh.*, p. 49-57.
- Shafer, M. W., and Roy, Rustum, 1954, Verbindungsbildung und Phasengleichgewicht in der Systemen  $\text{Cr}_2\text{O}_3\text{-H}_2\text{O}$ ,  $\text{Sc}_2\text{O}_3\text{-H}_2\text{O}$ , and  $\text{Tl}_2\text{O}_3\text{-H}_2\text{O}$ : *Zeitschr. Anorg. u. Allg. Chemie.*, v. 276, p. 275-288.
- Shannon, R. D., Rogers, D. B., and Prewitt, C. T., 1969, Chemistry of noble metal oxides—Synthesis and properties of  $\text{ABO}_3$  delafossite compounds: Central Research Department E. I. du Pont de Nemours and Co. Experimental Station, Wilmington, Del. Contr. 1616.
- Simon, A., Fischer, O., and Schmidt, T., 1930, Beiträge zur Kenntnis von Hydrogen über Chromoxyhydrate: *Zeitschr. Anorg. u. Allg. Chemie*, 185, p. 107.
- Stockley, G. M., 1955, The geology of British Guiana and the development of its mineral resources: *British Guiana Geol. Survey Bull.* no. 25, 102 p.
- Stroupe, J. D., 1949, An X-ray diffraction study of the copper chromites and of the "copper-chromium oxide" catalyst: *Am. Chem. Soc. Jour.*, v. 71, p. 569-572.
- Strunz, Hugo, 1970, *Mineralogische Tabellen*, 5th ed.: Leipzig, Akademische Verlagsgesellschaft Geest und Portig K.-G., 621 p.
- Svec, H. J., Flesch, G. D., and Capellen, J., 1962, The absolute abundance of the chromium isotopes in some secondary minerals: *Geochim. et Cosmochim. Acta*, v. 26, p. 1351-1353.
- Swanson, H. E., Fuyat, R. K., and Ugrinic, G. M., 1954, Standard X-ray diffraction powder patterns: *U.S. Natl. Bur. Standards Circ.* 539, v. 3, 73 p.
- Swanson, H. E., Gilfrich, N. T., and Ugrinic, G. M., 1955, Standard X-ray diffraction powder patterns: *U.S. Natl. Bur. Standards Circ.* 539, v. 5, 75 p.
- Swanson, H. E., Morris, M. C., Stinchfield, R. P., and Evans, E. H., 1962, Standard X-ray diffraction powder patterns: *U.S. Natl. Bur. Standards Mono.* 25, p. 4-5.
- Thamer, B. J., Douglass, R. M., and Staritzky, E., 1957, The thermal decomposition of aqueous chromic acid and some properties of the resulting solid phases: *Am. Chem. Soc. Jour.*, v. 79, p. 547-550.
- Thayer, T. P., Milton, Charles, Dinnin, Joseph, and Rose, H. J., Jr., 1964, Zincian chromite from Outokumpu, Finland: *Am. Mineralogist*, v. 49, p. 1178-1183.
- Tombs, N. C., Croft, W. J., Carter, J. R., and Fitzgerald, J. F., 1964, A new polymorph of  $\text{CrOOH}$ : *Inorg. Chemistry*, v. 3, p. 1791-1792.
- Torokin, A. N., Averbukh, T. D., Belova, N. V., and Rempel, P. S., 1968, The polymorphism of chromium oxyhydroxides obtained by reducing sodium chromate with hydrogen: *Russian Jour. Inorg. Chem.*, 13-15; translated from *Zhur. Neorg. Khim.* v. 13, no. 1, p. 27-38; also *Chem. Abstr.*, v. 68, p. 8753, Abstract 90659c (1968).
- Vuorelainen, Yrjö, Häkli, T. A., and Kataja, M., 1968, A hydrated oxide of chromium as a pseudomorph after eskolaite, Outokumpu, Finland: *Geol. Soc. Finland, Bull.*, v. 40, p. 125-129.
- Wiedersich, H., Savage, J. W., Muir, A. H., Jr., and Swarthout, D. G., 1968, On the composition of delafossite: *Mineralog. Mag.*, v. 36, p. 643-650.
- Yamaguchi, S., and Katsurai, T., 1967, Zur Kristallstruktur von Synthetischem  $\text{LaOOH}$ : *Naturwissenschaften*, v. 54, p. 514.
- Yund, R. A., and Kullerud, G., 1964, Stable mineral assemblages of anhydrous copper and iron oxides: *Am. Mineralogist* v. 49, nos. 5-6, p. 689-696.

---

---

PLATES 1-6

---

---

## PLATE 1

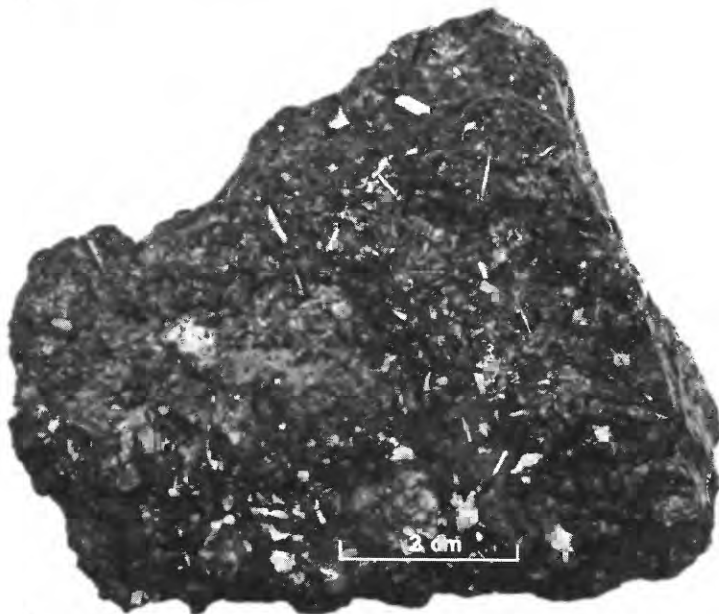
- FIGURE 1. Very large (8 cm) specimen of merumite. Exterior view showing botryoidal surface and inclusions of quartz.
2. Sawed face of merumite specimen in fig. 1 showing quartz inclusions.
  3. Exterior view of another very large (8 cm) merumite specimen showing botryoidal surface and quartz inclusions. 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).



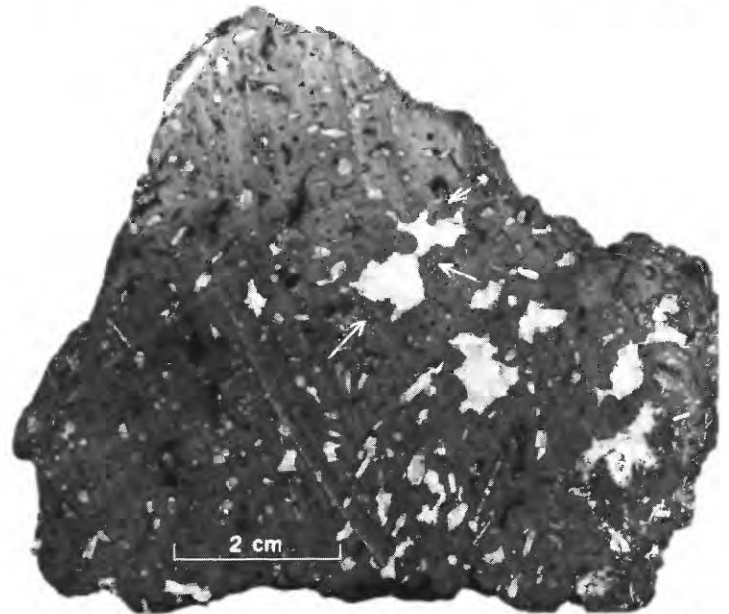
1



2



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.



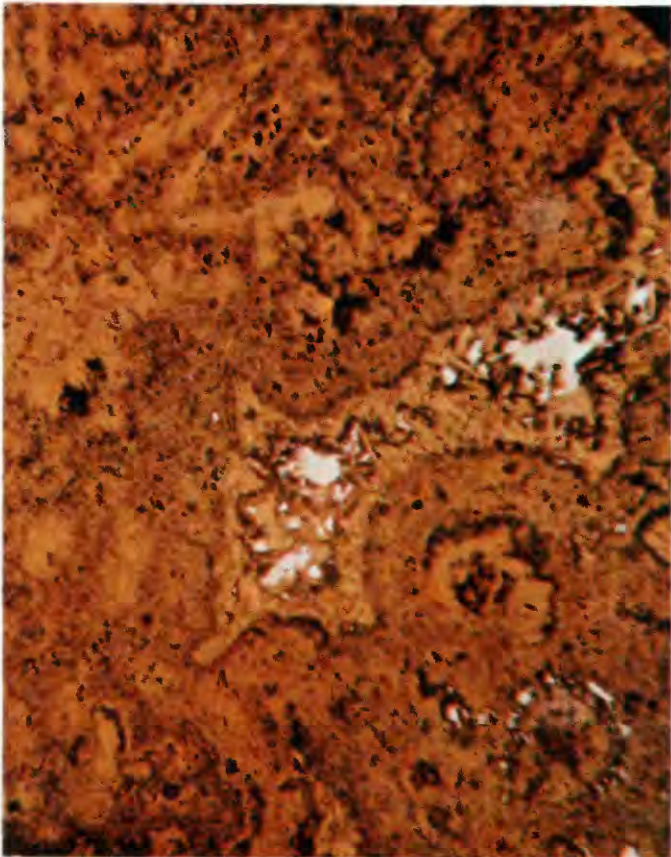


1

0.1 mm



2



3

0.1 mm

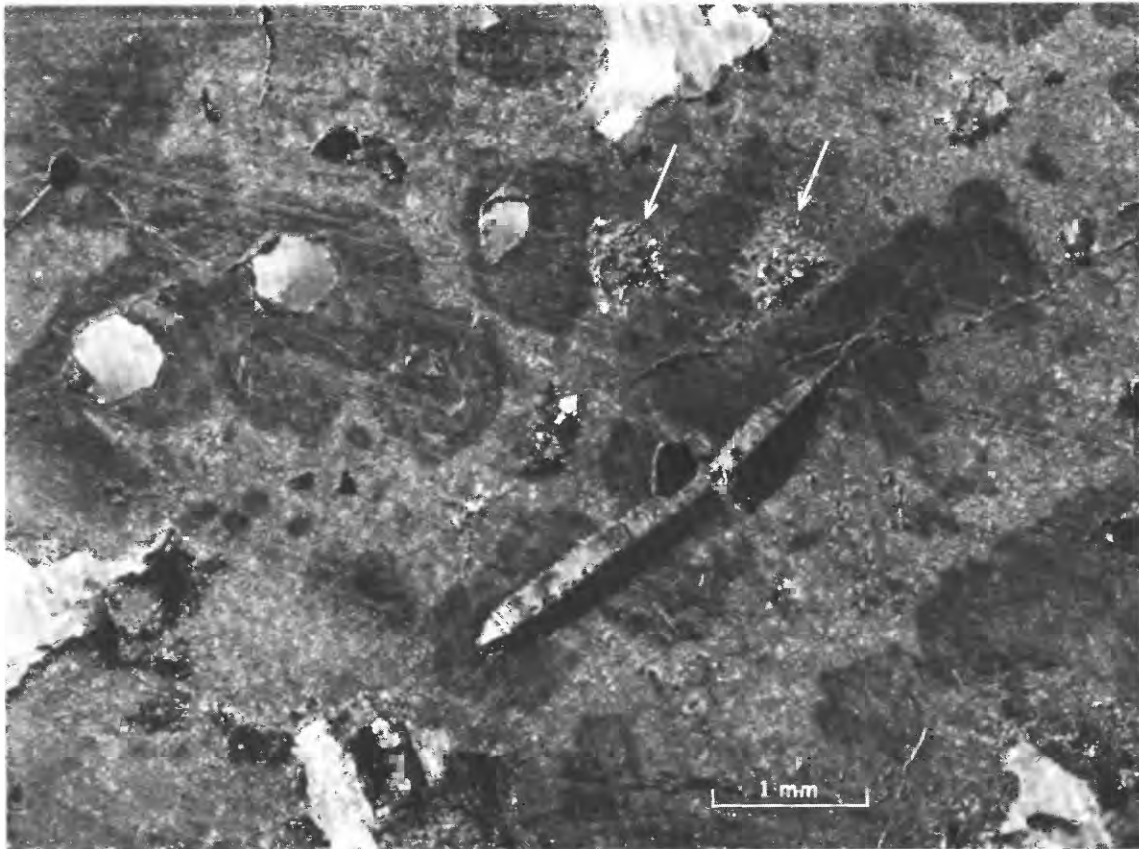


4

0.1 mm

### 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.



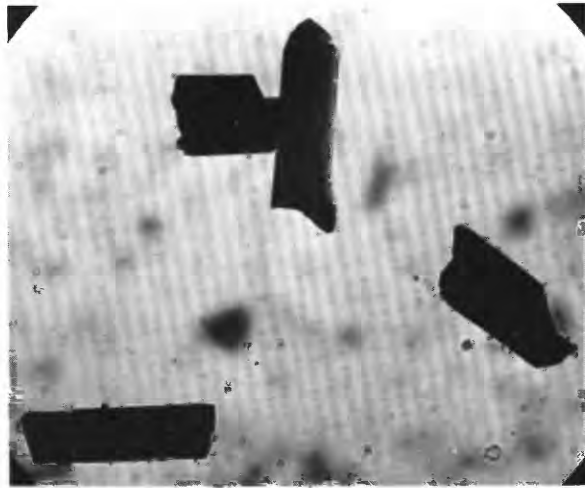
1



2

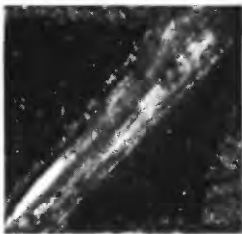
## PLATE 4

- 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  $\mu\text{m}$ . *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.



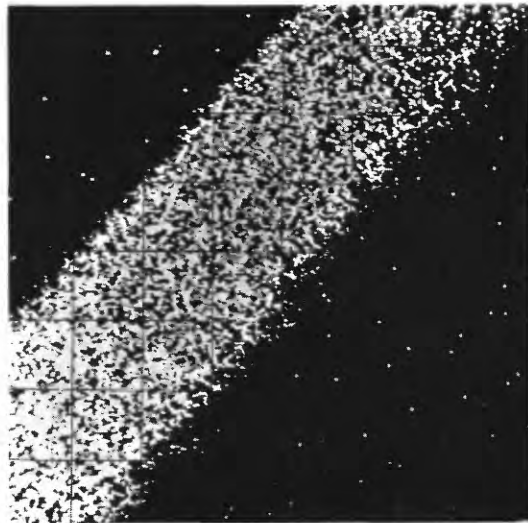
1

0.1 mm



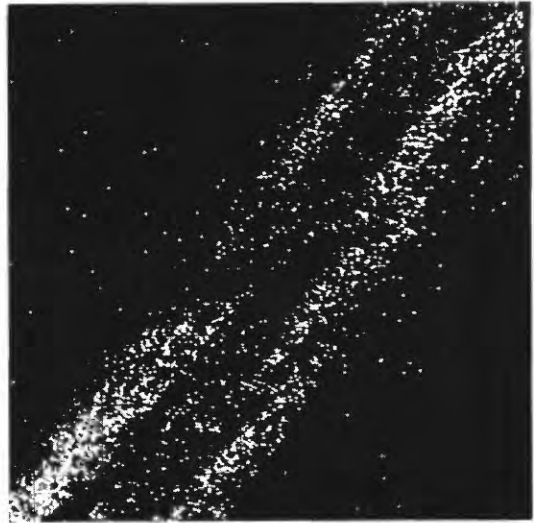
2A

70 μm



2B

70 μm



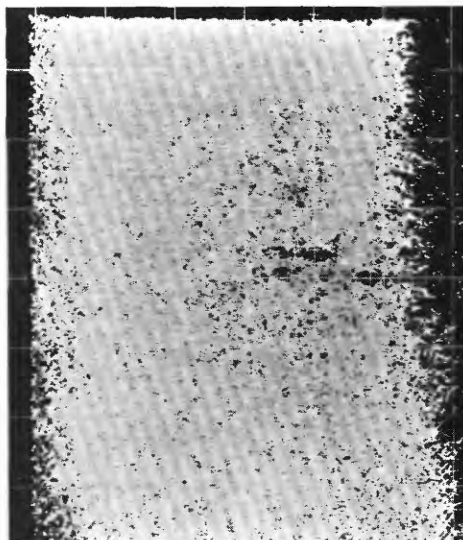
2C

70 μm



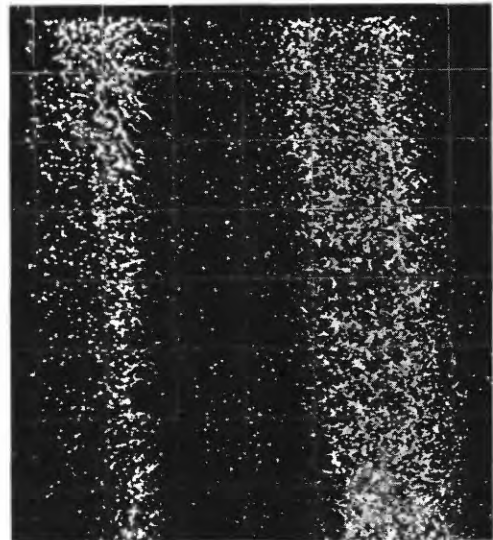
2D

70 μm



2E

70 μm



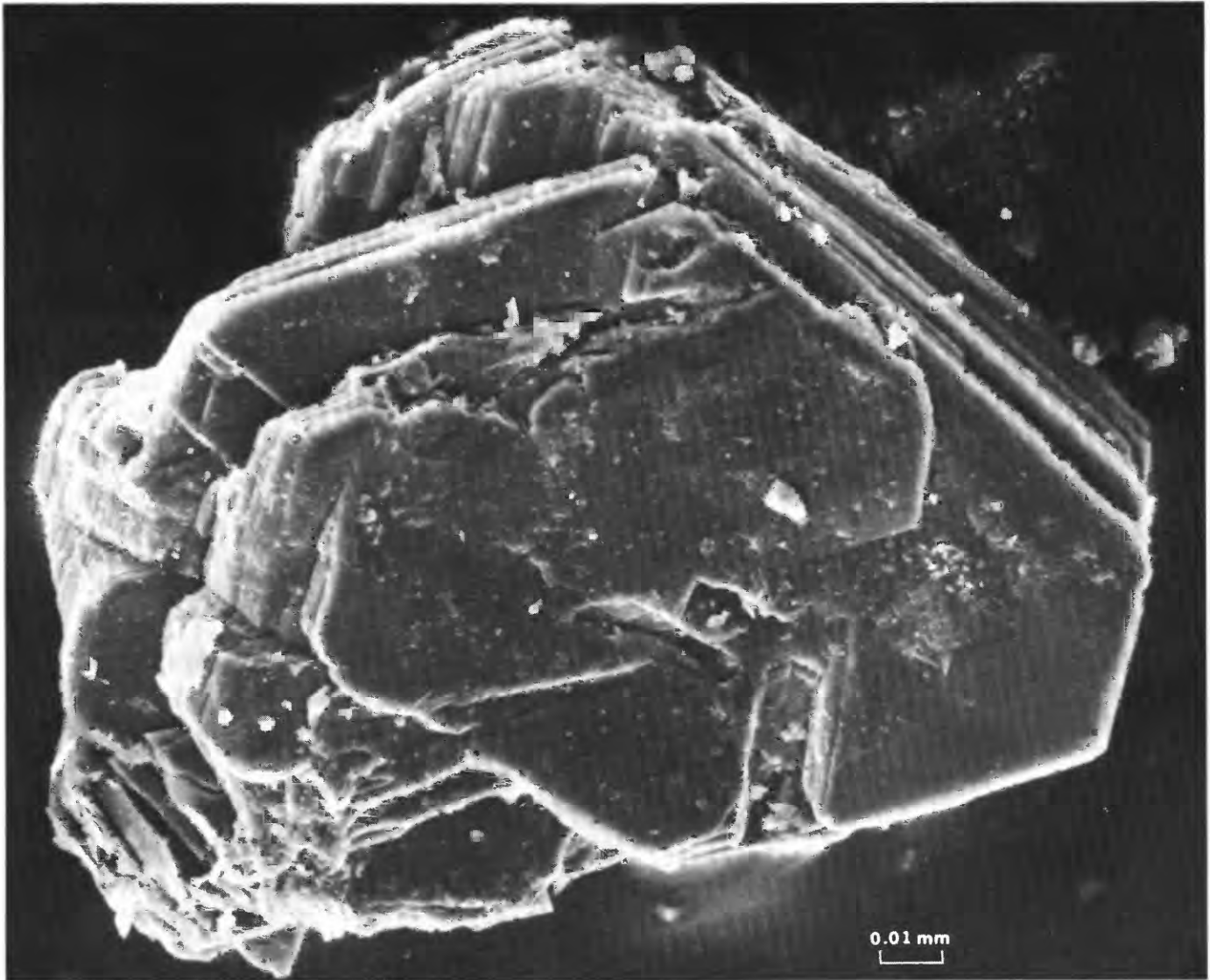
2F

70 μm

## 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  $\mu\text{m}$ . Taken by A. J. Tousimis.

1



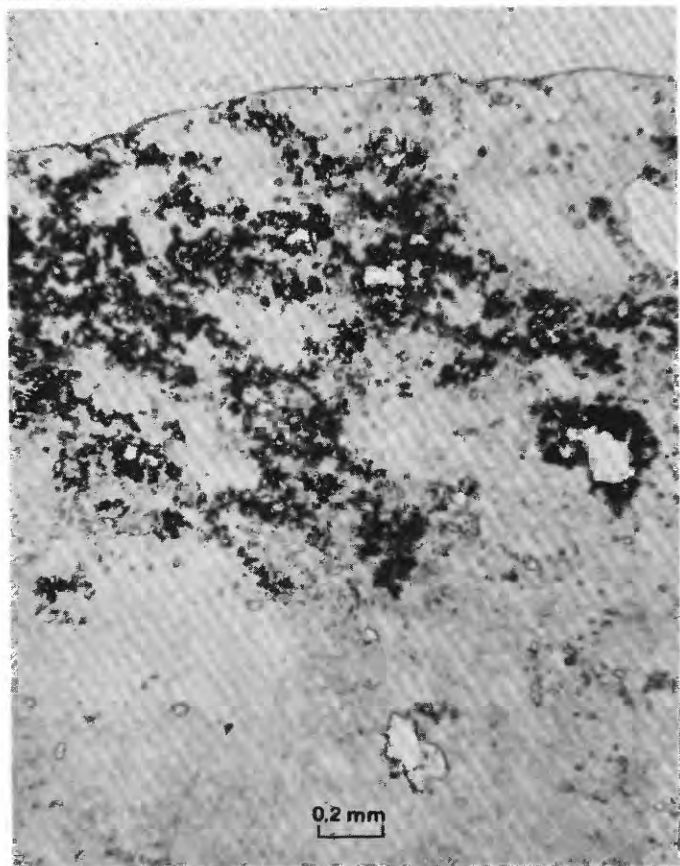
2



## 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.

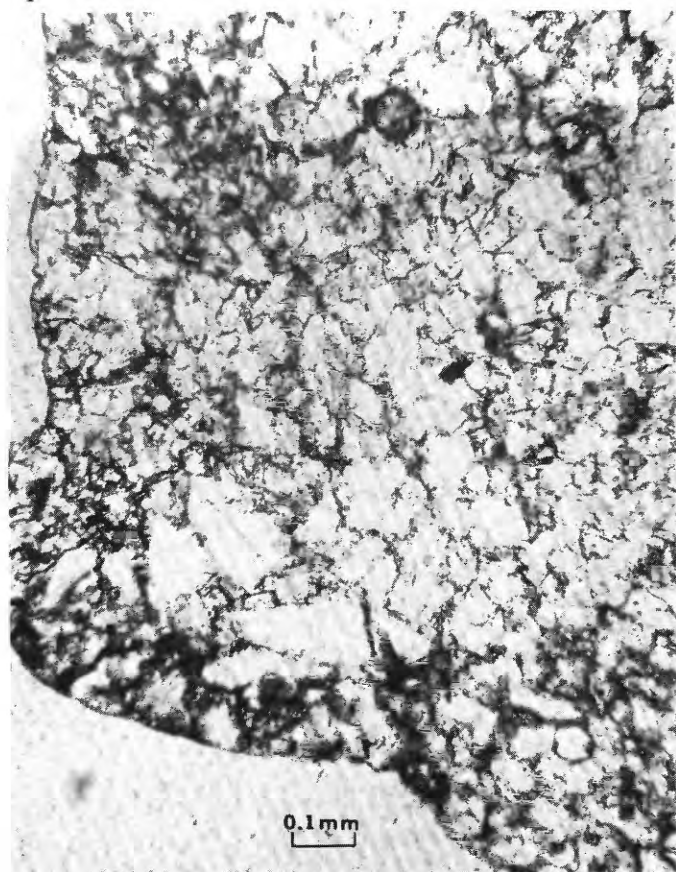




1



2



3



4