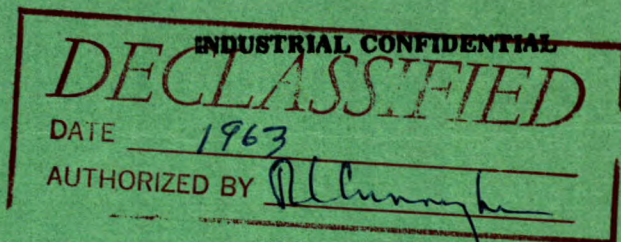


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**CANADA**

**DEPARTMENT OF MINES AND TECHNICAL SURVEYS**

**OTTAWA**

**MINES BRANCH INVESTIGATION REPORT IR 62-53**

**THE COMPOSITION OF PRODUCTS FROM  
THE GOLD-REFINING PROCESS OF  
MACASSA MINES LIMITED,  
KIRKLAND LAKE, ONTARIO**

by

**RONALD C. GARVIE & NORMAN F. H. BRIGHT**

**MINERAL SCIENCES DIVISION**

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Mines Branch Investigation Report IR 62-53

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Ronald C. Garvie\* and Norman F.H. Bright\*\*

- - -

SUMMARY OF RESULTS

A sample of material in the form of a bar produced during the pouring of gold ingots has been examined by X-ray diffraction, chemical, spectrographic and microscopic analyses. The bar, originally submitted as a speiss (i.e., a conglomerate of base metal arsenides, antimonides or tellurides) was, in fact, low in these elements. The gold content was quite low, although silver was a significant minor constituent. Copper was by far the most predominant element, appearing as the metal and also in the form of unknown compound(s). Altogether five phases were detected, only two of which were identified: metallic copper and silver. A sample of slag was also submitted along with the bar; this was shown to consist of copper manganite,  $\text{CuO} \cdot \text{Mn}_2\text{O}_3$ , cuprite  $\text{Cu}_2\text{O}$ , and some amorphous material. Other materials were present in smaller amount on the surface of the slag.

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CONTENTS

	<u>Page</u>
Summary of Results .....	i
Introduction .....	1
Experimental Techniques .....	1
1. X-ray Diffraction Examination.....	1
2. Spectrographic Analysis .....	2
3. Chemical Examination .....	2
4. Microscopic Examination and Photomicrography.....	2
Experimental Results .....	2
1. X-ray Diffraction .....	2
2. Spectrographic Examination .....	5
3. Chemical Analysis .....	5
4. Microscopic Examination .....	6
(a) Examination under High and Medium Magnification.....	6
(b) Examination under Low Magnification .....	6
Discussion of Results .....	9
Conclusions .....	10
Acknowledgements.....	10
Appendix: X-ray Diffraction, Microscopic and Spectroscopic Examination of Slag Material from Macassa Mines Limited ..	11
1. Introduction .....	11
2. Visual Examination.....	11
3. X-ray Diffraction Examination.....	12
4. Semi-Quantitative Spectrographic Examination .....	13
5. Microscopic Examination .....	14
6. Discussion .....	15

## INTRODUCTION

During July, 1960, a bar of material, weighing about 25 lb, was received in the Mineral Sciences Division, Mines Branch, Ottawa from Macassa Mines Limited, Kirkland Lake, Ontario. The sample was designated as a "speiss bar" and was accompanied by a sample of slag from the same source. It was requested that it be examined in this Division and the results of these examinations are outlined in this report; the work done on the slag sample is included in an Appendix (see pages 11 to 17).

The bar was originally submitted as a "speiss"--i.e., a conglomerate of base-metal arsenides or antimonides. However, since the nature of the bar was unknown at the time of receipt, it was considered better to describe it as a bar of impurities arising from the final stage (ingot formation) of the gold-refining operation. The bar was claimed to contain considerable precious metal values; the results of the examination, as will be seen, did not support this claim.

The bar as supplied for examination, was coated with a dark brownish-red glaze. The interior had a greyish metallic appearance. It was decided to examine the material by X-ray diffraction, semi-quantitative emission spectroscopy, chemical and microscopic analyses. The last-mentioned was done on polished sections taken from various parts of the bar.

## EXPERIMENTAL TECHNIQUES

### 1. X-ray Diffraction Examination

Samples were taken from various portions of the bar by filing material from it, followed by a thorough mixing and grinding of the filings to give representative samples. A 57.3 mm diameter Debye-Scherrer powder camera and filtered CoK radiation were used. The resultant powder diffraction patterns were interpreted, as well as possible, by measurement and comparison with data in the X-ray Powder Data File published by the American Society for Testing and Materials.

When interpreting X-ray diffraction patterns, the following limitations of the technique must be borne in mind. Crystalline constituents that are present in quantity less than about 5% of the total will probably not be detected and those in quantity less than about 2% will almost certainly

not be detected. Any amorphous material cannot be identified, and even its presence can be detected only when a substantial amount occurs. In this investigation, the relative abundance of the constituents present was assessed merely on the basis of the relative strengths of their diffraction patterns and, hence, this information should be considered as approximate only.

## 2. Spectrographic Analysis

A portion of the representative sample described above was examined by semi-quantitative emission spectroscopy to determine the nature and approximate abundance of the main metallic elements present.

## 3. Chemical Examination

A further portion of the representative sample was analysed quantitatively for certain common cations and anions.

## 4. Microscopic Examination and Photomicrography

For this analysis, nine polished sections were made from various areas in the bar. These were selected systematically in order to obtain reasonably complete coverage of the entire bar. The sections were examined at high, medium and low magnifications, i.e., 2000 X, 350 X and 28 X.

Two photomicrographs were made of representative regions, one at 2000 X and the other at 350 X. Leitz "Panphot" equipment was used for the photomicrography.

# EXPERIMENTAL RESULTS

## 1. X-ray Diffraction

The X-ray diffraction examination of the representative sample gave the following results:

Major constituent(s): Unidentified #1.

Minor constituent: Copper.

The detailed results (i.e., intensities and lattice spacings) are listed in Table 1. The reported intensities are relative to the strongest line measured on the film that was assessed at an arbitrary value of 10.

TABLE 1

X-ray Diffraction Results of Representative Sample of  
Macassa Mines Limited Bar

(The main diffractions of copper metal, taken from the ASTM Index are given for comparison purposes.)

Line No.	Intensity (estimated visually)	d-values (A)	Copper	
			Intensity	d-values (A)
1	3	3.48		
2	4	3.15		
3	1	2.457		
4	5	2.087	10	2.088
5	10	2.042		
6	10	1.940		
7	2	1.805	4.6	1.808
8	1	1.761		
9	1	1.408		
10	2	1.278	2.0	1.278
11	1	0.9217		
12	2	0.9089		
13	< 0.5	0.8985		

It can be shown that, neglecting lines 4, 7 and 10, which can be attributed to the presence of some copper, five of the remaining lines, namely 1, 3, 5, 8 and 9, form a cubic sequence. Hence, the non-copper lines either are due to two materials at least, of which one, giving rise to lines 1, 3, 5, 8 and 9, has a primitive cubic structure with a cell edge of about 3.50A, or, more likely, are due to one material, having possibly a tetragonal or hexagonal structure.

Samples were also taken from the top and bottom sections of the bar and examined by X-ray diffraction, with the following results:

Top Section

- |   |   |
|---|---|
| a) Representative material<br>(two specimens) | <u>Major:</u> Unidentified material<br>#1. (The films were<br>identical).   |
| b) White and metallic<br>material in cavities | <u>Major:</u> Silver metal.<br><u>Minor:</u> Copper; unidentified<br>material #2.<br><u>Trace:</u> Unidentified material<br>#1. |

Bottom Section

- |  |   |
|--|---|
| a) Shiny metallic material<br>(1st specimen) | <u>Major:</u> Copper<br><u>Small minor:</u> Unidentified<br>material #3.                                      |
| b) Shiny metallic material<br>(2nd specimen) | <u>Predominant:</u> Copper<br><u>Trace:</u> Unidentified material<br>#3.                                      |
| c) Soft bronze-coloured<br>material only     | <u>Predominant:</u> Copper<br><u>Trace:</u> Unidentified material<br>#3.                                      |
| d) Soft black material<br>only               | Copper--only crystalline<br>constituent detected. Large<br>amount of amorphous material<br>present (carbon?). |

## 2. Spectrographic Examination

Semi-quantitative emission spectroscopy gave copper as the principal constituent of the bar, with the minor constituents being as listed below.

<u>Element</u>	<u>%(by weight)</u>	<u>Element</u>	<u>%(by weight)</u>
Ag	5.0	As	0.2
Ca	1.0	B	0.2
Si	0.9	Mg	0.2
Mn	0.9	Ti	0.17
Zn	0.6	P	0.1
Al	0.6	Ba	0.05
Fe.	0.6	V	0.03
Na	0.4	Ni	0.03
Pb	0.3		

## 3. Chemical Analysis

Chemical analysis for the elements commonly found in such a context as the present sample, yielded the following results:

<u>Element</u>	<u>%(by weight)</u>	<u>No. of Determinations</u>
Cu	59.56	3
Ag	3.43	4
S	6.66	3
As	0.11	1
Au	0.02	4
Si	0.26	1

Note:- No analyses were conducted for nickel or antimony, although these elements are often present in a speiss, since the spectrographic analysis had shown that the nickel content was very low and that antimony was not detectable at all.



#### 4. Microscopic Examination

##### (a) Examination under High and Medium Magnification

This study revealed the presence of six phases, listed in Table 2. These six phases were seen to be present in all the samples examined, although their relative abundances varied randomly from sample to sample.

Figures 1 and 2 show two photomicrographs of polished sections of a portion of the Macassa bar. Only four of the phases described in Table 2 can be discerned here. The background mass seen in Figure 1 is phase (A). The large light islands are phase (B), while the dark intergranular material is phase (C). Phase (D) is seen as light-coloured flecks distributed throughout phase (C). Figure 2 shows phase (C) in more detail and at higher magnification. It is seen to consist of very small worm-like, dark islands packed close together. Phases (E) and (F) can be detected only by their colour and hence are not distinguishable on these photomicrographs.

##### (b) Examination under Low Magnification

Under the low-power microscope (28 X), grains of native copper were readily visible. The grains appeared to be randomly distributed throughout the matrix phase. No steady variation of copper content as a function of direction or of position in the bar could be discerned.

TABLE 2

Phases Detected by Microscopic Examination

Phase	Abundance	Description of Phase		Identification of Phase
		Colour	Distribution	
A	Major	Light blue-grey	Matrix phase in which others are distributed.	Unidentified
B	Minor	Reddish-gold	Randomly distributed as islands throughout (A).	Copper
C	Minor	Dark grey	Myrmekitic (worm-like); distributed along grain boundaries of (A).	Unidentified
D	Trace	Silvery grains	Found within phase (C)	Silver
E	Trace	Yellow grains	Found within phase (C)	Unidentified
F	Trace	Dark blue grains	Found within phase (C)	Unidentified



**Figure 1. Polished Section of Macassa Bar**  
**Magnification: 350 X**  
**(Straight lines are polishing scratches)**



**Figure 2. Polished Section of Macassa Bar**  
**Magnification: 2000 X**  
**(Straight lines are polishing scratches)**

## DISCUSSION OF RESULTS

The spectrographic and chemical analyses generally agree that the bar consists of a copper-rich complex, low in precious metals and those elements which would classify it as a speiss or matte, i.e., S, As, Sb, Te. Using the results given by these two types of analysis, one can account for about 75% of material of the bar. Since no large amount of any other metal was detected spectroscopically, the remaining 25% is, presumably, oxygen.

The X-ray diffraction results, given in Table 1, indicate that free copper metal is present only as a significant minor constituent of the bar. This finding is confirmed by the microscopic examination reported in Table 2. On the other hand, the chemical and spectrographic analyses indicate that copper is by far the most abundant element present in this bar. Hence, there must be some unidentified compound of copper present as a major constituent, presumably the matrix material, phase (A), reported in Table 2. The unknown compound is probably an oxide or oxy-salt of copper, to account for the above-mentioned 25% of the bar not included in the analyses. However, no agreement can be found between the X-ray data for any known compound of copper and those recorded in Table 1.

The microscopic examination shows that the relative abundances of the various phases is such that one might expect phases (A), (B) and (C) to register their patterns in an X-ray diffraction examination of a representative sample of the bar. Table 1 shows that the three strongest lines of Cu metal were, in fact, observed at such an intensity as would correspond to Cu being present as a significant minor constituent. Ten lines thus remain unaccounted for in Table 1. It has been stated that five of these ten lines can be interpreted as arising from a material of primitive cubic structure, having a cell-edge  $a_0 = 3.50 \text{ \AA}$  approx. This material could possibly be the phase (C) observed in the microscopic examination, since this appeared to have about the same relative abundance as that of the free copper metal. On this basis, the six remaining diffraction lines as yet unaccounted for would be assigned to the matrix phase, which must be, according to the arguments given above, an unidentified copper oxide or oxy-salt. These six lines do not correspond with the published data for any known copper compound. However, it is considered more likely that the phase (A) is either tetragonal or hexagonal in structure and accounts for all the unidentified lines and that phase (C) is amorphous. This phase could conceivably be amorphous carbon; such a phase would not be detected either spectrographically or by X-ray diffraction by the technique adopted in this work. The evidence at present available does not permit an unequivocal identification of any of the phases present other than the metallic copper and silver.

## CONCLUSIONS

The bar of material from Macassa Mines Limited is a copper-rich complex, low in precious metals and those elements that would classify it as a speiss or matte. The copper appears to be present mainly as an unknown complex oxide or oxy-salt and to a minor extent as the free metal. Small amounts of free silver and other phases are present.

## ACKNOWLEDGEMENTS

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(An Appendix follows)  
(on pages 11 to 17. )

## APPENDIX

### X-ray Diffraction, Microscopic and Spectrographic Examination of Slag Material from Macassa Mines Limited

#### 1. Introduction

Accompanying the bar of material that forms the subject of the main body of this report was a sample of slag-like material, which was sent from Macassa with a view to its assisting in the identification of the materials in the bar itself. As will be seen later, the slag did not, in fact, prove to be of any assistance in the bar analysis, but, on the contrary, presented fresh problems of its own.

#### 2. Visual Examination

A visual examination of the slag sample showed that it appeared to consist of four different phases:

- (a) Black, shiny material that was very hard and vitreous and formed the main body of the slag;
- (b) brownish-grey material that coated certain areas of the surface of the slag, almost with the appearance of a mould-growth;
- (c) white, powdery material, deposited on certain surface areas;
- (d) black, brittle, needle-like crystals formed in hollows and irregularities in the surface of the slag.

These phases can be seen in Figure 3, which is a photograph of a portion of the slag taken at low magnification.

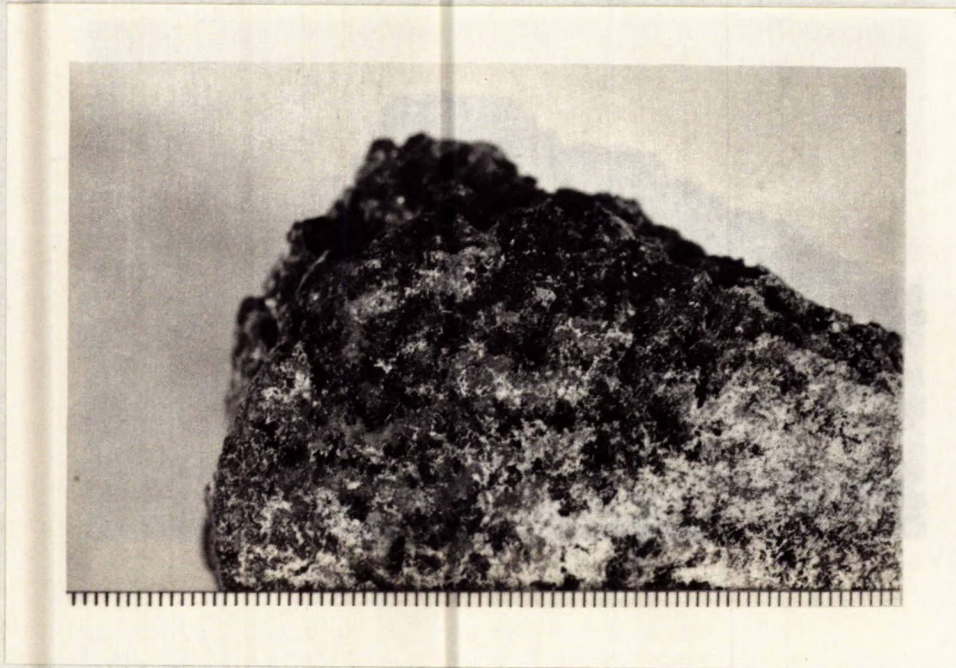


Figure 3. Photograph of Portion of Macassa Slag  
(Scale at lower edge of photograph is in millimetres)

### 3. X-ray Diffraction Examination

A specimen of each of the four phases listed above was subjected to X-ray diffraction examination. The results obtained are given in Table 3.

TABLE 3

X-ray Diffraction Results on Macassa Slag

Description of Phase	X-ray Findings
Black, shiny material	<p><u>Major:</u> Crednerite (<math>\text{CuO} \cdot \text{Mn}_2\text{O}_3 ?</math>)*  <u>Minor:</u> Cuprite (<math>\text{Cu}_2\text{O}</math>)                      Some amorphous material is present.</p>
Brownish-grey material on surface	<p><u>Major:</u> Sodium aluminum silicate (cubic with <math>a = 7.27 \text{ \AA}</math>)*  <u>Minor:</u> Crednerite, cuprite  <u>Trace:</u> Sodium tetraborate pentahydrate  <math>\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}</math>*</p>
White, powdery material	<p><u>Predominant:</u> Sodium tetraborate pentahydrate, <math>\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}</math></p>
Black, needle-like crystals (two specimens)	<p>Both samples were identical. Crednerite (<math>\text{CuO} \cdot \text{Mn}_2\text{O}_3 ?</math>)*</p>

\* See comments on page 15.

4. Semi-quantitative Spectrographic Examination

The results of the semi-quantitative X-ray emission spectrographic examination of the four different phases observed visually are given in Table 4.



TABLE 4

Semi-Quantitative Spectrographic Examination of Macassa Slag  
(Figures are in percentage by weight.)

Element	Black, shiny material	Grey material	White, powdery material	Black needles
Ba	0.1	0.3	0.2	0.1
Si	3	M.C.	2	6
B	0.4	2	M.C.	2
Al	1	3	1	2
Mn	1	2	1	4
Fe	0.2	2	0.5	0.6
Cr	0.01	Tr	N.D.	0.06
V	0.06	0.2	N.D.	0.08
Mo	0.004	N.D.	N.D.	Tr?
Ca	2	6	2	3
Cu	M.C.	M.C.	1	M.C.
Ag	0.1	0.1	0.1	0.1
Na	3	M.C.	M.C.	6
Ni	0.004	Tr	Tr	0.009
Zn	3	6	N.D.	4
Pb	0.5	0.7	0.3	0.4
Ti	0.07	0.3	0.2	0.2
Co	Tr	N.D.	N.D.	N.D.
Zr	0.003	N.D.	N.D.	Tr

Notes:- (a) "M.C." denotes "major constituent".  
 (b) "N.D." denotes "none detectable".  
 (c) "Tr" denotes "trace".

5. Microscopic Examination

A thin section of the slag was prepared. A photomicrograph of this section is shown in Figure 4.



Figure 4. Photomicrograph of Thin Section of Macassa Slag  
Magnification: 270 X

## 6. Discussion

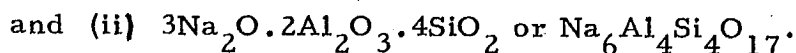
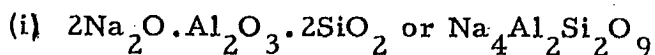
The X-ray diffraction results obtained with the various materials taken from the slag require some amplification.

The "crednerite" identified in several of the samples, including the needle-like crystals, is based upon the best available check with information given in the ASTM Powder Data File and is found in the latest set of cards, issued in 1961. The formula given above,  $\text{CuO} \cdot \text{Mn}_2\text{O}_3$  (?), is that quoted on the ASTM card (including the "?", indicating that it is not definitely known.) The variations of the diffractions obtained in the present case from those given on the ASTM card consist of small shifts in d-spacings, corresponding to a slightly different cell size. The intensities are, in general, in good agreement. The spacing variations could well be caused by some degree of substitution of other metals in the  $\text{CuO} \cdot \text{Mn}_2\text{O}_3$  lattice, which is entirely possible under the present circumstances. The general appearance of the crystals, which are, presumably, the needle-like phase visible in Figure 4, is in accord with the meagre information published concerning this material in Dana's "System of Mineralogy".

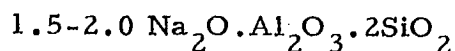
The dendritic formations visible in Figure 4 will, therefore, be the cuprite,  $\text{Cu}_2\text{O}$ , phase. The optical properties of this material, again,

are consistent with the known data for this mineral.

With regard to the sodium aluminum silicate mentioned in Table 3, it was found that two compounds of this type with identical d-spacings, but with slightly differing intensities were included in the latest set of ASTM Powder Data cards; both compounds are cubic with unit-cell dimension  $a = 7.27 \text{ \AA}$ . The formulae quoted for these two compounds are



It was not possible to distinguish which of these two compounds was present in the sample. A consultation of the latest  $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  phase equilibrium diagram in the relevant composition region shows that the above compositions lie within the phase area of the compound carnegieite, which has the formula  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ . This material will tolerate considerable excess  $\text{Na}_2\text{O}$  in solid solution and still retain the carnegieite structure. It is therefore considered that the material encountered in the present instance is a soda-rich carnegieite-type solid solution, having the formula



The white, powdery material that was identified as being sodium tetraborate pentahydrate,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$  has presumably been formed by partial dehydration of the decahydrate, borax  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ , which is used as a flux in the gold smelting operation.

Thus it has been possible to identify the crystalline components associated with this slag to a reasonable degree of completeness. The material which forms the matrix visible in Figure 4 is, presumably, the amorphous material referred to in Table 3. From the spectrographic data given in Table 4, it would appear likely that the slag and the crystals obtained from it are of essentially the same composition. It is thus likely that the slag is a copper-manganese-rich oxide in the glassy or amorphous condition. This slag also contains significant amounts of Na, Ca, Zn, B and Si. It is therefore entirely likely that, included in this glassy phase, are certain complex borates and silicates, both of which types of compound are known to be strongly glass-forming materials.

While it has been possible to give a reasonably complete description of the nature of the slag, it will be seen that the information thereby obtained is of little or no value in elucidating the nature of the phases present in the "speiss" bar which forms the original subject of this investigation. Owing to a lack of standard materials for X-ray and optical reference, it has not been possible to identify many of the constituents found in the bar. The very fine-grained texture encountered in this material precluded separation of the various constituents in sufficient quantities for the chemical analyses or other diagnostic procedures that would be required for complete identification.

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