UNIVERSITY OF TORONTO STUDIES
GEOLOGICAL SERIES, No. 46

---

# CONTRIBUTIONS TO CANADIAN MINERALOGY, 1941

From the
DEPARTMENT OF MINERALOGY AND PETROGRAPHY
UNIVERSITY OF TORONTO
and the
WALKER MINERALOGICAL CLUB

THE UNIVERSITY OF TORONTO PRESS
TORONTO, CANADA
1941

LONDON:
HUMPHREY MILFORD
OXFORD UNIVERSITY PRESS

# TABLE OF CONTENTS

*At Professor Parsons's Request the Papers*
*Contributed to this Issue have been*
*Arranged for Publication*
*by Professor Peacock*

# STUDIES OF MINERAL SULPHO-SALTS:
# V—MENEGHINITE FROM ONTARIO AND TUSCANY

By L. G. BERRY, *Research Enterprises Ltd., Toronto*
and D. A. MODDLE, *Ontario Department of Mines*

The difficulty of identifying an uncommon ore mineral in a polished section is considerably increased if the unknown is one of several species which are similar in crystal habit and chemical composition, and consequently similar in microscopic appearance and chemical behaviour. This applies to the slender prismatic to needle-like sulphantimonites of lead among which are jamesonite, boulangerite, zinckenite, and meneghinite. The properties of these minerals, as observed in polished sections (Short, 1940) are not identical, it is true; nevertheless the positive identification afforded by exactly matched *x*-ray powder photographs is a welcome support to the microscopic determination. The results of detailed studies of jamesonite and boulangerite, with indexed powder patterns, were given in recent papers (1940a, 1940b). *X*-ray measurements, but no powder data, have been given for zinckenite by Vaux and Bannister (1938). A closer study of meneghinite was suggested by the identification of a mineral from Ontario with the type meneghinite from Tuscany (Peacock and Berry, 1940, p. 61).[1]

## MENEGHINITE FROM ONTARIO

Meneghinite has been reported in Frontenac County, Barrie Township, lots 5 and 9, concession IX, and in Hastings County, at Marmora Township, S. Emmons lot (Johnston, 1915, p. 155). Massive material in quartz and dolomite, from Marble Lake, Barrie Township, was analysed by Harrington (1882).

The material which was recently identified as meneghinite was collected by Dr. V. B. Meen from lot 8, concession II, Anglesea Township, Lennox and Addington County, from a rusty quartz vein (6 to 30 inches wide) with low gold values (0.2 oz./ton). The

---

[1] The polished sections and powder photographs were studied by Berry; the unit cell was determined by Moddle. Professor Peacock has supervised the work and has assisted us in bringing it to completion.

mineral occurs embedded in vein quartz, in flattened and somewhat distorted, galena-white, columnar masses up to 10 mm. long and 5 mm. wide, showing the brilliant side pinakoidal cleavage and an occasional indication of the basal cleavage.

In a polished section, cut transversely to the columnar structure, the mineral is galena-white and strongly anisotropic, light tan, brown, to blue-grey. Etch reactions: $HNO_3$, quickly stains iridescent and etches brown with very slight effervescence; HCl, slight brownish stain, some areas negative; KCN, $FeCl_3$, KOH, $HgCl_2$, negative. A microchemical test for copper (potassium mercuric thiocyanate), on clean material, gave a good positive reaction. The $x$-ray powder photograph (Fig. 2) is identical with that given by crystallized meneghinite from Bottino Mine, Tuscany (Fig. 1).

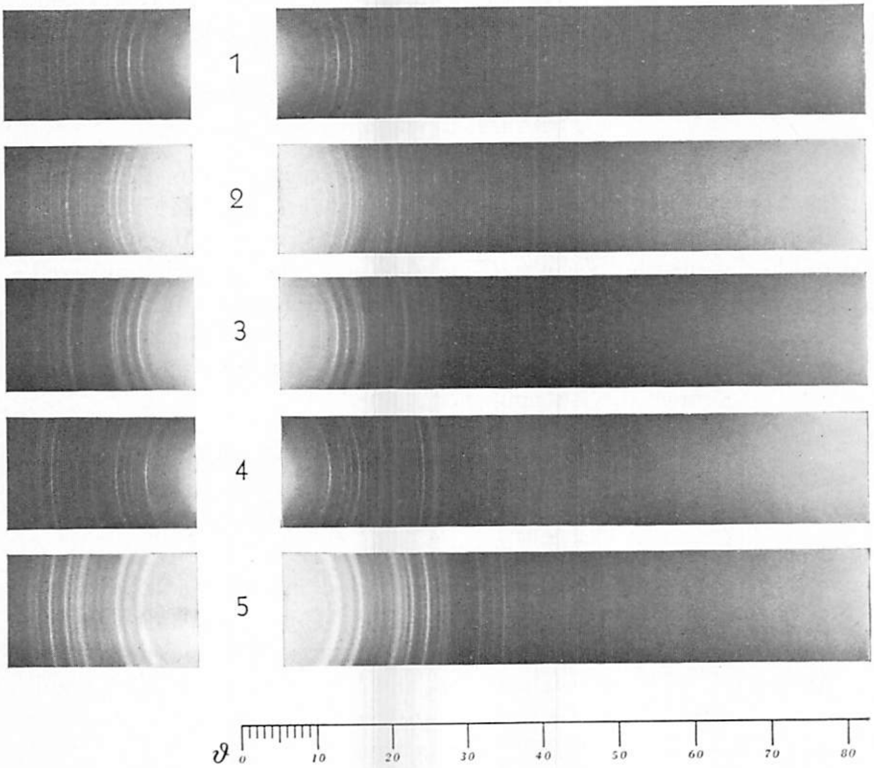
## MENEGHINITE FROM TUSCANY

The existing rather extensive knowledge of meneghinite rests almost entirely on observations on prismatic crystals from the original locality, Bottino Mine, Tuscany, Italy. Palache (1938) recently confirmed the orthorhombic symmetry and revised the geometrical crystallography with reference to the unit cell determined by Richmond. From one of the existing analyses Richmond obtained the cell content $Pb_{13}Sb_7S_{23}$, and advanced this composition in place of the previously accepted composition $4PbS.Sb_2S_3$.

### *Physical Properties*

Our material (Univ. Toronto, Dept. Min., A/1803) consists of a quantity of loose needles and prisms from 0.1 to 1.0 mm. in thickness, agreeing in appearance with existing descriptions. The basal cleavage, which is evidently difficult, was clearly observed, but no faces were seen terminating the deeply striated prismatic crystals.

A polished section of some of the thicker crystals, cut about parallel to the direction of elongation, is galena-white and moderately strongly anisotropic, light tan, brown, to blue-grey. Hardness B+ (slightly greater than galena, distinctly less than chalcopyrite). Specific gravity, 6.42 (Peacock), 6.40 (F. G. Smith). Etch reactions: $HNO_3$, in 10 seconds stains iridescent and etches brown with very little effervescence; HCl, KCN, $FeCl_3$, KOH, $HgCl_2$, negative. The microchemical test with potassium mercuric thiocyanate clearly showed copper in a solution of the clean crystals.



FIGS. 1-5.—*X*-ray powder photographs with copper radiation (nickel filter); camera radius, $360/4\pi$ mm.; full-size reproductions of contact prints. FIG. 1.—Meneghinite, Bottino Mine, Tuscany. FIG. 2.—Meneghinite, Anglesea Township, Ontario. FIG. 3.—Jamesonite, Poopo, Bolivia. FIG. 4.—Boulangerite, Príbram, Bohemia. FIG. 5.—Zinckenite, Wolfsberg, Harz.

The microscopic characters of meneghinite from Ontario and Tuscany are thus practically alike, and they are substantially the same as those given by Schneiderhöhn and Ramdohr (1931) and by Short (1940), who likewise used material from Bottino Mine. Without the positive microchemical test for copper, which is noted by Short as the distinguishing character of meneghinite, this mineral could hardly be distinguished from boulangerite (1940b) under the microscope. The microscopic characters of meneghinite are also close to those of jamesonite, which may be distinguished, however, by a positive microchemical test for iron (1940a), and to those of zinckenite.

### *Structural Crystallography*

Since the existing structural data for meneghinite (Hofmann, 1935; Hiller, 1938; Richmond, 1938) do not agree, a re-determination of the unit cell seemed desirable. For this purpose the necessary single-crystal photographs (Figs. 6-8) were made, with unfiltered iron radiation, using a thin unterminated needle from Bottino. Our films, like those of Richmond, show orthorhombic symmetry. Careful measurements[2] led to the following dimensions of the unit cell, as compared with published values (Å):

| | MODDLE | RICHMOND | HILLER | HOFMANN |
|---|---|---|---|---|
| $a_0$.......... | 11.36±0.02 | 11.29 | 11.70 | — |
| $b_0$.......... | 24.04±0.04 | 23.78 | ($c_0$) 13.70 | — |
| $c_0$.......... | 8.26±0.03 | 4.12 | ($b_0$) 8.25 | 8.30 |

Our values for the true lattice period in the needle-axis ($c_0$) is close to those of Hiller and Hofmann. This value is required by a very weak first layer line which was apparently overlooked by Richmond. The new values for $a_0$ and $b_0$ exceed those of Richmond by amounts which are slightly greater than our limits of error. Our cell volume ($V_0 = 2256$ Å$^3$) is thus perceptibly greater than twice that of Richmond ($2V_0 = 2206$ Å$^3$). As in the case of jamesonite and boulangerite, the unreliable method used by Hiller (1938), led him to erroneous values for the transverse lattice period of meneghinite.

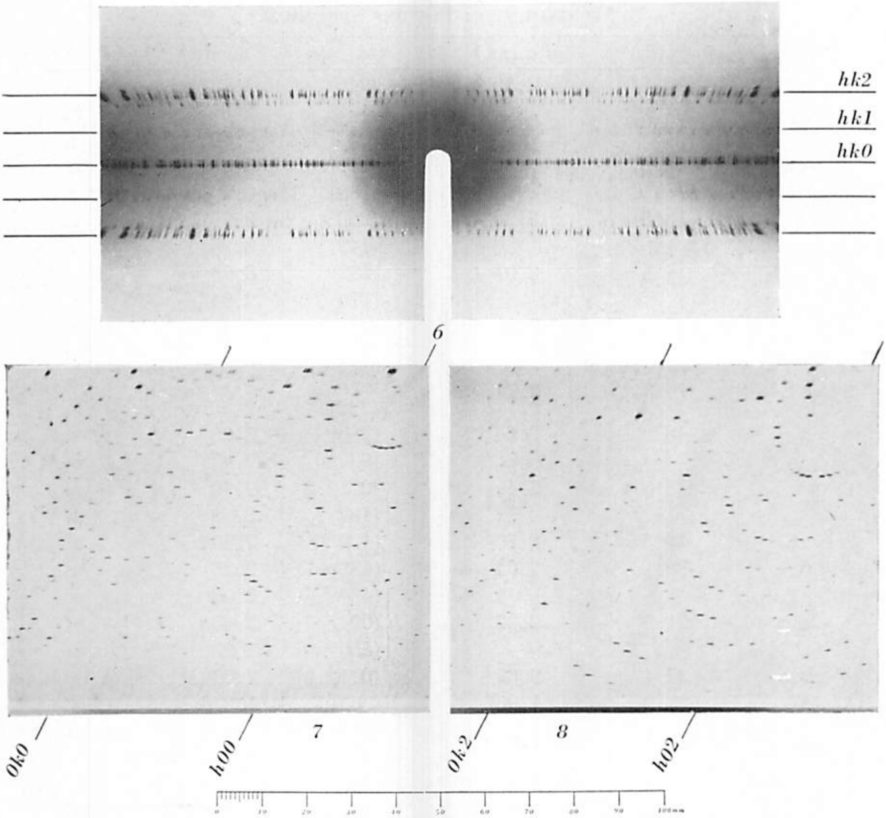
The first layer of meneghinite is too weak to be resolved on a Weissenberg photograph and thus we cannot obtain the space-group

---

[2] Since large cell dimensions must be determined as accurately as possible, in order to obtain the cell contents correctly, the instrumental corrections currently used in this laboratory were recently verified from rotation and Weissenberg photographs on an elongated cleavage rhombohedron of Iceland spar, 0.2 mm. thick, rotating about a cleavage edge.

of the true unit cell. The second layer, however, yields the following systematic omissions, with reference to the pseudo-cell ($a_0$, $b_0$, $c_0/2$):

($hkl$) present in all orders
($0kl$) present only with $k$ even
($h0l$) present only with ($h+l$) even
($hk0$) present in all orders



FIGS. 6-8.—*X*-ray photographs of a needle of meneghinite from Bottino, with unfiltered iron radiation; camera radius $360/4\pi$ mm. The axis of rotation is the needle axis [001]. FIG. 6.—Rotation photograph showing the weak first layer /$hk1$/. FIG. 7.—Zero Weissenberg /$hk0$/. FIG. 8.—Second layer Weissenberg /$hk2$/.

If meneghinite is holohedral the pseudo-cell thus provides still another example of the space-group $D_{2h}^{16}$, in the orientation *Pbnm.*

### *Powder Photographs*

The identical *x*-ray powder patterns of meneghinite from Ontario

TABLE 1

MENEGHINITE: POWDER SPECTRUM

| $I$(P,Cu) | $\theta$(Cu) | $d$(meas.) | ($hkl$) | $d$(calc.) | $I$(S,Fe) |
|---|---|---|---|---|---|
| vw | 10.8° | 4.10 Å | (240) | 4.13 Å | m |
| vs | 12.0 | 3.70 | (122) | 3.69 | m |
| | | | (320) | 3.65 | m |
| vvw | 12.6 | 3.52 | (132) | 3.49 | vs |
| vvs | 13.5 | 3.29 | (170) | 3.29 | s |
| | | | (260) | 3.27 | s |
| | | | (142) | 3.26 | s |
| vvw | 14.5 | 3.07 | (232) | 3.08 | vs |
| vvs | 15.3 | 2.91 | (270) | 2.94 | s |
| | | | (242) | 2.92 | s |
| | | | (180) | 2.91 | m |
| s | 16.3 | 2.74 | (312) | 2.79 | s |
| | | | (322) | 2.74 | m |
| s | 16.9 | 2.64 | (280) | 2.66 | s |
| vw | 18.6 | 2.41 | (082) | 2.43 | m |
| | | | (0.10.0) | 2.40 | m |
| | | | (182) | 2.38 | m |
| vvw | 19.5 | 2.30 | (422) | 2.30 | s |
| w | 20.1 | 2.24 | (432) | 2.25 | vs |
| vs | 21.8 | 2.07 | (480) | 2.06 | s |
| | | | (004) | 2.06 | – |
| | | | (550) | 2.05 | m |
| vvw | 22.4 | 2.02 | (0.12.0) | 2.00 | s |
| s | 23.0 | 1.967 | (560) | 1.976 | s |
| vw | 23.4 | 1.935 | (392) | 1.936 | m |
| | | | (542) | 1.932 | s |
| s | 24.2 | 1.875 | (600) | 1.870 | s |
| vw | 24.6 | 1.846 | (482) | 1.846 | s |
| m | 25.3 | 1.799 | (0.12.2) | 1.802 | s |
| vw | 25.6 | 1.779 | (562) | 1.783 | s |
| | | | (3.12.0) | 1.775 | s |
| vw | 26.3 | 1.735 | (3.11.2) | 1.725 | s |
| s | 26.6 | 1.717 | (0.14.0) | 1.717 | s |
| vw | 27.1 | 1.687 | (1.14.0) | 1.698 | s |
| vw | 30.0 | 1.537 | (2.15.0) | 1.543 | s |

| $I$(P,Cu) | $\theta$(Cu) | $d$(meas.) | $I$(P,Cu) | $\theta$(Cu) | $d$(meas.) |
|---|---|---|---|---|---|
| vw | 30.9° | 1.497Å | w | 45.5° | 1.078Å |
| vw | 31.3 | 1.480 | w | 46.4 | 1.061 |
| vw | 32.3 | 1.438 | w | 48.3 | 1.029 |
| vw | 32.7 | 1.423 | w | 49.3 | 1.014 |
| s | 33.4 | 1.396 | w | 50.3 | 0.999 |
| vw | 35.4 | 1.327 | w | 54.3 | 0.947 |
| m | 38.3 | 1.240 | w | 58.7 | 0.900 |
| s | 40.0 | 1.196 | w | 63.9 | 0.856 |
| vw | 42.4 | 1.140 | s | 66.1 | 0.841 |
| vw | 43.4 | 1.119 | m | 71.3 | 0.812 |
| vw | 44.3 | 1.101 | | | |

$I$(P,Cu)—Intensity of powder line (copper radiation). $\theta$(Cu)—Corrected glancing angle. $d$(meas.)—Measured spacing. (*hkl*)—Indices of the powder ring. $d$(calc.)—Calculated spacing. $I$(S,Fe)—Intensity of single crystal spot (iron radiation).

and Tuscany are reproduced with standard patterns of jamesonite, boulangerite, and zinckenite in Figs. 1-5. These fine-lined patterns reproduce poorly in reduced half-tones; the full-size reproductions of contact prints given here should show the distinct differences between the three patterns and serve as a practical means of distinguishing the three species.

To verify the pattern of meneghinite the powder lines have been indexed as far as $\theta = 30°$, beyond which the indexing is necessarily uncertain owing to the large cell dimensions. In this case, as in previous cases, the list of diffractions and relative intensities given by the single crystal photographs, was indispensable in assigning the indices to the powder lines.

## *Geometrical Crystallography*

Our knowledge of the crystallography of meneghinite rests mainly on the nearly simultaneous studies of Krenner (1883) and Miers (1884) who both recognized the orthorhombic symmetry of the crystals but took different settings. Dana (1892) gave Miers's results, with the axes *a* and *b* interchanged. Goldschmidt (1897) took the average of Miers's and Krenner's elements in Krenner's setting. Ungemach (1923) proposed a new setting which proves to be the same as ours. Palache (1938) transformed Goldschmidt's elements to Richmond's structural setting. The transformation formulas leading from the old settings to the new setting (Ungemach; Berry and Moddle) are as follows:

| | |
|---|---|
| Krenner (Goldschmidt): | ½00/010/00½ |
| Miers: | ¼00/010/00½ |
| Dana: | 0¼0/100/00½ |
| Palache (Richmond) | 100/010/002 |

The existing independent axial ratios, in the new setting, are much alike, the new $x$-ray values being remarkably close to those of Miers:

$a:b:c=0.4747:1:0.3428$ (Krenner)
$0.4726:1:0.3433$ (Miers)
$0.4750:1:0.3466$ (Richmond, $x$-ray)
$0.4726:1:0.3436$ (Moddle, $x$-ray)

Palache gave a list of the established forms of meneghinite, with Goldschmidt's angles, adding two new forms, φ(0.24.11) and ω(7.21.1), which he observed on crystals from Bottino. This form list is given below together with the indices in the new setting.

TABLE 2

MENEGHINITE: ESTABLISHED FORMS

| PALACHE | UNGEMACH BERRY and MODDLE | PALACHE | UNGEMACH BERRY and MODDLE | PALACHE | UNGEMACH BERRY and MODDLE |
|---|---|---|---|---|---|
| *c*(001) | (001) | *k*(310) | (310) | μ(211) | (212) |
| *b*(010) | (010) | *y*(032) | (034) | *p*(241) | (121) |
| *a*(100) | (100) | *d*(021) | (011) | δ(0.24.13) | (0.12.13) |
| *e*(160) | (160) | *o*(083) | (043) | φ(0.24.11) | (0.12.11) |
| *R*(140) | (140) | *v*(041) | (021) | *q*(24.0.11) | (12.0.11) |
| *S*(130) | (130) | *n*(101) | (102) | λ(24.24.13) | (12.12.13) |
| *l*(380) | (380) | *W*(403) | (203) | σ(24.24.11) | (12.12.11) |
| *f*(5.12.0) | (5.12.0) | *V*(201) | (101) | ρ(24.48.11) | (12.24.11) |
| *T*(120) | (120) | *u*(111) | (112) | ψ(24.48.13) | (12.24.13) |
| *g*(340) | (340) | β(221) | (111) | *X*(24.72.13) | (12.36.13) |
| *i*(780) | (780) | *t*(121) | (122) | π(24.96.13) | (12.48.13) |
| *m*(110) | (110) | *s*(131) | (132) | ω(7.21.1) | (7.21.2) |
| *h*(520) | (520) | *r*(141) | (142) | | |

In the new notation the symbols of the pinakoids and the vertical prisms are unchanged; those of the simple series of important forms *nutsr* become more complicated, while those of the remarkable "aberrant" forms $\delta \varphi q \lambda \sigma \rho \psi X \pi$ are systematically simplified. It was the simplification of the symbols for the aberrant forms which suggested the new setting to Ungemach.

Palache's recent measurements confirmed a number of the aberrant forms and placed the reality of these forms beyond question. They are clearly not vicinals to the nearest planes with simple indices, nor can they be explained by twinning. Unlike the aberrant forms of calaverite (Goldschmidt, Palache, and Peacock, 1931) those of meneghinite can be related to two superlattices which are in rational, if complicated, relation to the principal lattice. This possibility is evident in the gnomonic projection, Fig. 9, in which it can be seen that $\delta \lambda \psi X \pi$ lie on one gnomonic supernet (1), while $\varphi q \sigma \rho$ lie on the other (2). The aberrant forms can, of course, only give the relative lengths of the possible superlattice periods. The simplest integral superlattice periods which will give complete simplification of the aberrant forms are:

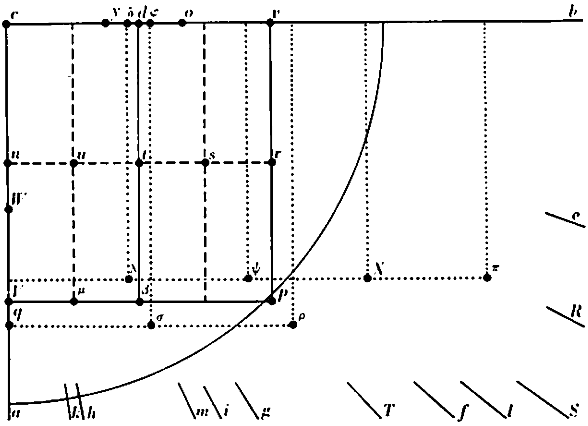


FIG. 9.—Meneghinite: gnomonic projection of the established forms. The gnomonic net in full lines corresponds to the structural lattice (Ungemach; Berry and Moddle); the net in broken lines represents the pseudo-lattice (Palache; Richmond); the dotted nets correspond to the hypothetical superlattices.

(1): $a_1 = 13a,\ b_1 = 13b,\ c_1 = 12c$
(2); $a_2 = 11a,\ b_2 = 11b,\ c_2 = 12c$

With reference to these superlattices the aberrant forms receive the following symbols:

| (1) | (2) |
|---|---|
| $\delta(0.12.13) \longrightarrow (011)$ | $\varphi(0.12.11) \longrightarrow (011)$ |
| $\lambda(12.12.13) \longrightarrow (111)$ | $q(12.0.11) \longrightarrow (101)$ |
| $\psi(12.24.13) \longrightarrow (121)$ | $\sigma(12.12.11) \longrightarrow (111)$ |
| $X(12.36.13) \longrightarrow (131)$ | $\rho(12.24.11) \longrightarrow (121)$ |
| $\pi(12.48.13) \longrightarrow (141)$ | |

Such superlattices are not inconceivable, in view of the relation of the true cell ($a$, $b$, $c$) to the pseudo-cell ($a'$, $b'$, $c'$,) recently obtained from $x$-ray measurements on sartorite (Peacock and Berry, 1940, p. 64): $a = 4a'$, $b = 20b'$, $c = c'$. However, this suggestion of two superlattices in meneghinite must remain a speculation until it is tested by $x$-ray photographs, with suitable radiation, on a crystal showing the aberrant forms.

In regard to the definitive geometrical setting of meneghinite we do not feel that the change to the structural setting is imperative. The development of the principal forms is clearly related to the pseudo-cell and therefore Palache's setting may properly be retained for the geometrical presentation.

### *Composition and Cell Content*

In deriving the cell content $Pb_{13}Sb_7S_{23}$ and proposing this composition in place of $Pb_4Sb_2S_7 = 4PbS.Sb_2S_3$, Richmond relied on the analysis (vom Rath, 1867) which showed the "smallest amount of impurity." In the eight available analyses of meneghinite[3] (Doelter, 1926, p. 447) the reported elements, in addition to Pb, Sb, S, are Cu in appreciable amounts, Fe in generally much smaller quantities, and rarely minute proportions of Ag and As. The fact that Cu enters the composition of meneghinite was established by Short (1940, p. 117), who notes that copper is readily detected microchemically on a specimen from Bottino, and it is confirmed by our microchemical tests on clean material from Ontario and Tuscany. In deriving the cell content of meneghinite, Cu and the generally very small amounts of other elements are

---

[3] **One analysis, showing Zn 4.94, is neglected as unreliable.**

therefore retained and the analyses are reduced to atoms per unit cell, using the highest reliable specific gravity (6.43), given by Loczka (in Krenner, 1883) for Bottino, and by Flink (1910) for Sweden (Table 3).

TABLE 3

MENEGHINITE: ANALYSES

EXPRESSED IN ATOMS PER UNIT CELL

| | Fe | Cu | Ag | Pb | Sb | As | S |
|---|---|---|---|---|---|---|---|
| 1 ......... | 0.55 | (4.90) | ..... | 25.16 | 13.94 | ..... | 48.11 |
| 2 ......... | 0.37 | 0.55 | ..... | 26.78 | 13.62 | ..... | 47.79 |
| 3 ......... | .... | 1.92 | ..... | 26.20 | 14.25 | ..... | 47.06 |
| 4 ......... | 0.40 | 2.18 | ..... | 25.70 | 13.91 | ..... | 50.38 |
| 5 ......... | (4.16) | .... | ..... | 25.76 | 14.61 | ..... | 46.83 |
| 6 ......... | 0.48 | 3.96 | 0.09 | 26.23 | (12.28) | 0.27 | 48.56 |
| 7 ......... | 0.11 | 1.90 | 0.07 | 26.31 | 14.11 | ..... | 46.52 |
| 8 ......... | 0.11 | 1.67 | ..... | 26.47 | 13.66 | ..... | 47.86 |
| Average.... | 0.29 | 2.06 | ..... | 26.08 | 14.01 | ..... | 47.86 |

1. Bottino; anal. Bechi, 1852 (Doelter, no. 1). 2. Bottino; anal. vom Rath, 1867 (Doelter, no. 3). 3, 4. Saxony; anal. Frenzel, 1870 (Doelter, nos. 4, 5). 5. Bottino; anal. Martini and Funaro, 1876 (Doelter, no 6). 6. Bottino; anal. Loczka, 1883 (Doelter, no. 7). 7. Ontario; anal. Harrington, 1882 (Doelter, no. 8). 8. Sweden; anal. Mauzelius, 1910 (Doelter, no. 9).

Omitting the three values in brackets as out of line, the average cell content is very close to:

$$Cu_2Pb_{26}Sb_{14}S_{48} = Cu_2S.26PbS.7Sb_2S_3$$

As recognized by Palache (1938) there is no isostructural relation between meneghinite and jordanite, for which one of us recently obtained the monoclinic unit cell with $a_0=8.89$, $b_0=31.65$, $c_0=8.40$ Å; $\beta=118°21'$, containing $27PbS.7As_2S_3$ (Peacock and Berry, 1940, p. 59).

## SUMMARY

Meneghinite from lot 8, concession II, Anglesea Township, Lennox and Addington County, Ontario, is identified with crystals (sp. gr. 6.42-6.40) from Bottino Mine, Tuscany, by microscopic study and *x*-ray powder photographs. A re-determination of the orthorhombic lattice of meneghinite from Bottino gives the unit cell with $a_0=11.36$, $b_0=24.04$, $c_0=8.26$ Å. A well-marked pseudo-cell with $a_0$, $b_0$, $c_0/2$ has the symmetry of the space-group $D_{2h}^{16} = Pbnm$. Microchemical tests on clean material confirm the presence of Cu, and the available analyses lead to the cell content and composition, $Cu_2S.26PbS.7Sb_2S_3$. The $x$-ray powder photograph is indexed and reproduced with photographs of jamesonite, boulangerite, and zinckenite, to aid in the future identification of the needle-like sulph-antimonites of lead. The dominant forms of meneghinite are controlled by the pseudo-lattice; the aberrant forms suggest the existence of two superlattices which are rationally related to the structural lattice.

## REFERENCES

BERRY, L. G. (1940a): Studies of mineral sulpho-salts: II—Jamesonite from Cornwall and Bolivia—*Min. Mag.*, vol. 25, pp. 597-608.

———— (1940b): Studies of mineral sulpho-salts: III—Boulangerite and "epiboulangerite"—*Univ. Toronto Studies, Geol. Ser.*, no. 44, pp. 5-19.

DANA, E. S. (1892): *System of Mineralogy*, ed. 6—New York.

DOELTER, C. and LEITMEIER, H. (1926): *Handbuch der Mineralchemie*, vol. 4, pt. 1—Dresden and Leipzig.

FLINK, G. (1910): Bidrag till Sveriges mineralogi—*Ark. Kemi, Min. Geol.*, vol. 3, no. 35, 166 pp.

GOLDSCHMIDT, V. (1897): *Krystallographische Winkeltabellen*—Berlin.

———— PALACHE, C., and PEACOCK, M. A. (1931): Über Calaverit—*N. Jahrb. Min., Beil.-Bd.* (A), vol. 63, pp. 1-58.

HARRINGTON, B. J. (1882): On some minerals new to Canada—*Trans. Roy. Soc. Canada*, vol. 1, sec. 3, pp. 79-81.

HILLER, J. E. (1938): Röntgenographische Bestimmungsmethoden und Untersuchung der Bleispeissglanze—*Zeits. Krist.* (A), vol. 100, pp. 128-156.

HOFMANN, W. (1935): Ergebnisse der Strukturbestimung komplexer Sulfide—*Zeits. Krist.* (A), vol. 92, pp. 161-185.

JOHNSTON, R. A. A. (1915): A list of Canadian mineral occurrences—*Geol. Surv. Canada*, Mem. 74.

KRENNER, J. A. (1883): Ueber den Meneghinit von Bottino—*Földtani Közlöny*, vol. 13, p. 297 [Abs. *Zeits. Kryst.*, vol. 8, pp. 622-624, 1884].

MIERS, H. A. (1884): On the crystalline form of meneghinite—*Min. Mag.*, vol. 5, pp. 325-331.

PALACHE, C., RICHMOND, W. E., and WINCHELL, H. (1938): Crystallographic studies of the sulpho-salts: baumhauerite, meneghinite, jordanite, diaphorite, freieslebenite—*Am. Mineral.*, vol. 23, pp. 821-836.

PEACOCK, M. A. and BERRY, L. G. (1940): Röntgenographic observations on ore minerals—*Univ. Toronto Studies, Geol. Ser.*, no. 44, pp. 47-69.

SCHNEIDERHÖHN, H. and RAMDOHR, P. (1931): *Lehrbuch der Erzmikroskopie*, vol. 2—Berlin.

SHORT, M. N. (1940): Microscopic determination of the ore-minerals—*U.S. Geol. Surv.*, Bull. 914.

UNGEMACH, H. (1923): Sur les formes cristallines de notation compliquée—*Zeits. Krist.*, vol. 58, pp. 150-171.

VAUX, G. and BANNISTER, F. A. (1938): The identity of zinckenite and keeleyite —*Min. Mag.*, vol. 25, pp. 221-227.

# TRISOCTAHEDRAL GARNET FROM THE BLACK LAKE REGION, QUEBEC

By J. D. H. DONNAY and CARL FAESSLER
*Université Laval, Quebec*

## INTRODUCTION

Trisoctahedral garnets from West Thetford Mines, Quebec, have been described by A. L. Parsons (1935). They showed the remarkable combination of forms: $r\{233\}$, $d\{011\}$, $n\{112\}$, in order of decreasing importance. One of us had previously encountered this curious morphological development on garnets from the Black Lake region, which were described[1] at the 1934 meeting of the Association canadienne-française pour l'Avancement des Sciences (Faessler, 1935). These garnets were, at that time, identified as uvarovite. Inasmuch as Parsons determined his garnet, on the basis of a chemical analysis by W. F. Green, as andradite 78.74—grossularite 18.45—diopside 2.91, and in view of the fact that Black Lake is only four miles distant from West Thetford, a redetermination of the Black Lake garnets was necessary. This will be found in Part I.

Parsons, in his paper, stresses the rarity in garnets of the trisoctahedron $\{233\}$ and the even greater scarcity of the trisoctahedron $\{122\}$, as compared with the almost universal occurrence of the rhomb-dodecahedron and the trapezohedron $\{112\}$. To account for these facts, he offers an explanation based on structural considerations. In recent years, however, it has been possible to obtain a better understanding of the morphological development of crystals, thanks to the Generalization of the Law of Bravais (Donnay and Harker, 1937). A treatment of the garnet morphology in the light of the generalized law will be found in Part II.

## I. THE BLACK LAKE GARNETS
(C.F.)

The crystals are pale gooseberry green in colour, up to 13 mm. in the largest dimension. The dominant form is the trisoctahedron

---

[1] *Erratum:* The symbol of the trapezohedron mentioned in that paper should read $\{211\}$, instead of $\{221\}$.

{233}, truncated by fairly wide faces of the rhomb-dodecahedron and by small faces of the trapezohedron {112}.

The specific gravity is 3.69, determined on a fragment of about 15 mg. (Berman torsion balance). A crystal fragment fuses easily before the blowpipe (*F* 3.5) to a glass globule, black and magnetic. The borax bead obtained in the oxidizing flame is brownish when hot and colourless when cold, proving the presence of iron and the absence of chromium. Optically, the fragments show the anomalous, low birefringence, so often found in calcium garnets; the index of refraction is higher than 1.74 (medium relief in methylene iodide).

These characters suffice to rule out uvarovite and all other garnets except andradite and grossularite. The strong magnetism of the fused fragments indicates a preponderance of andradite. The specific gravity (3.69) is very close to the weighted average of Parson's determinations for the various fractions of his sample (1935, p. 33). The average is 3.75 for the isotropic material, and 3.64 for the whole sample (anisotropic portion included).

In conclusion, the Black Lake garnets are essentially andradite, and their composition may be very close to that given by Parsons for the crystals from West Thetford Mines.[2]

## II. GARNET MORPHOLOGY

(J.D.H.D.)

*Data.*—The two dominant forms are known to be the trapezohedron {112} and the rhomb-dodecahedron {011}. They are the forms observed on artificial crystals: {112} on $Mn_3Al_2Si_3O_{12}$ and {011} on $Ca_3Fe_2Si_3O_{12}$, the only two cases known with certainty of artificial reproduction of garnets (Groth, 1908). Natural crystals show many more forms. In Goldschmidt's *Atlas* (1918) 94 crystal drawings of garnets are figured; leaving out the illegible figures and those for which the locality is unknown, 65 remain, which can provide the necessary data for a statistical study of relative form importance.

---

[2] Amber coloured crystals, reported as grossularite, showing the trisoctahedron {233} have been figured from American Chrome Pit, in the Black Lake district, by Poitevin and Graham (1919). The habit is dodecahedral, {011} modified by {112} and {233}, about equally developed, also {123}, {012}, {023}, {001}, as narrow truncations.

The most frequent forms are indeed $\{011\}$ and $\{112\}$, found on 53 and 45 figures, from 29 to 24 localities respectively. As to size, $\{112\}$ is larger than $\{011\}$ on 24 figures, while $\{011\}$ is larger than $\{112\}$ on 30 figures; $\{112\}$ is larger than $\{011\}$ in 10 localities, $\{011\}$ is larger than $\{112\}$ in 16 localities. These two forms are about equally important. The next group of forms comprises $\{123\}$, $\{001\}$, $\{012\}$, found on 15, 13, 16 figures, from 8, 9, 7 localities, respectively. Then come $\{233\}$, found on 6 figures, from 3 localities; and $\{134\}$, 5 figures and 2 localities.

All other forms are rare. The octahedron, however, which has the reputation of being very scarce in garnets, is figured 13 times, from 6 localities. This may seem strange, but one should take into account the authors' natural propensity for figuring rare forms on their drawings. In view of the baffling rarity of the octahedron, this form must have been searched for more diligently and figured each time it was found. The perusal of the *Atlas* must be done critically, and the consensus of mineralogists on the scarcity of the octahedron cannot be ignored.

*Discussion.*—Several concepts have been used to explain the relative importance of crystal forms. (1) The *simplicity of indices*—the smaller the indices $h$, $k$, $l$, the more important the form $\{hkl\}$. (2) Later the sum of the squares of the indices, $\Sigma=(h^2+k^2+l^2)$, was used as a measure of form importance—the smaller this sum, the more important the form. In the isometric system, and if the lattice is simple cubic (or primitive), the square root of $\Sigma$ is inversely proportional to the spacing between successive $hkl$ lattice planes; in this case, therefore, using $\Sigma$ or $\sqrt{\Sigma}$ amounts to using the Law of Bravais—the larger the interplanar spacing, the more important the form. Parsons's explanation can be shown to belong in here. (3) The preceding concepts introduce no difference between isometric crystals, which should consequently all show the same forms in the same order of importance. The Law of Bravais was able to distinguish three different sequences of forms, one for each lattice mode. The halving of an interplanar spacing produced by the lattice centring (*e.g.*, the halving of the 001 planes in the case of a body-centred lattice) can be expressed by doubling the indices (the cube becoming 002 in the above example). The multiple indices, introduced in the expression $\sqrt{h^2+k^2+l^2}$, lead to a larger value, in keeping with the decreased importance of the form. (4) Other possible halvings, or quarterings, of interplanar spacings are due to the space-group symmetry. These are taken into account by the Generalized Law, which distinguishes 17 different form sequences or *aspects* in the isometric system (Donnay and Harker, 1940).

The space-group of garnets, found by *x*-ray methods, is known to be $O_h^{10}-Ia3d$. The conditions imposed on the indices, in this case, are as follows:

*hkl*.........condition I : sum even
0*kl*.........condition Q: all even
*hhl*.........condition J: half-sum even
001.........to be multiplied by 4; hence, 004

The list of forms, arranged in the order of decreasing interplanar spacings (increasing values of $\sqrt{\Sigma}$), or decreasing theoretical importance, is (using the multiple indices): 112.022.123.004.024. 233.134.125.(235.116).026.145.136.444.345.046. This theoretical order is quite satisfactory. The first seven forms are the dominant forms of the species, and their relative importances reflect the observed facts. The extreme rarity of the trisoctahedron {122}, emphasized by Parsons, is well accounted for, since it must be written {488} in order to satisfy the condition J (*half-sum even*). The agreement between theory and observation cannot be expected to hold for the rare forms. I have found no record, for instance, of the forms {125}, {116}, {136}, {345}, which appear on the theoretical list.[3] The forms {235}, {026}, {444}, {046}, on the other hand, are uncommon, but valid forms. Finally, a dozen or more forms, mentioned by Dana (1892), are inexplicable, as they do not conform to the space-group criteria. They must be exceedingly rare, or small, or both, since they are not to be found on the published crystal drawings.

Not only is it possible to predict the order of importance of the forms to be expected in a given space-group, but conversely the space-group can be predicted from the morphological development (Donnay, 1938). In the isometric system this can be done in two ways. (1) The 17 possible aspects are listed, once and for all.

---

[3] Although {116} is not mentioned in the literature, Rath (1878) has reported a form {2.2.11}.

The aspect is selected that fits the observed morphology best. In the case of garnets, three aspects give top ranks to {112} and {011}, but two of them place {013} third, and one of those places {222} fourth, before {123}, which is a much more common form. Only one aspect is satisfactory, namely aspect *Ia*d*, which uniquely defines the space-group $O_h^{10}-Ia3d$. (2) The extinction criteria, that is to say the conditions which are imposed on the indices by the space-group symmetry, are reconstructed from the observed relative importance of the forms. In the case of garnets, the most common general forms observed are {123} and {134}. This establishes the condition **I** (*sum even*) for the {*hkl*} forms. The other two possible criteria are **F** (*all odd or all even*), which would require {135} and {246}, and **P** (*no condition*), which would demand {123} and {124}. The forms {0*kl*} can be listed in order of decreasing importance as follows: {011}, {012}, {013}. Hence, the criterion can only be **P** or **Q** (*all even*). But {012} is less important than {112}, it must therefore be written {024}; likewise {013} must be written {026} in order adequately to express its importance, smaller than that of {123}. The criterion for the forms {0*kl*} is thus **Q** (or **F**). The fact that {112} and {233} are the most common {*hhl*} forms determines the criterion **J** (*half-sum even*) for these forms. As to the cube, it can only be written {004} to account for its importance, smaller than that of {112}. The complete extinction symbol **IFJ4** is thus reconstructed;[4] it uniquely defines the space-group.

One last point is noteworthy. The space-group being determined by morphological means, the minimum number of like atoms that can be placed in the cell is also known. Knowing the chemical formula, it is therefore possible to find the smallest number of molecules that the cell can accommodate. Assuming it to be the number of molecules really contained in the cell, it is easy to predict the absolute value of the cell edge $a_0$. The unit-lengths thus obtained may be compared with the old *topic parameters* (which defined a cell arbitrarily made to contain one gram-molecule), but their significance is considerably enhanced (Donnay, 1940). For grossularite garnet, for instance, using the formula $Ca_3Al_2Si_3O_{12}$

---

[4] Note that the symbols Q (*all even*) and F (*all odd or all even*) are equivalent in the case of the forms {0*kl*}.

and the specific gravity 3.6, the minimum number of molecules per cell is 8, and the cell edge can be predicted to be 11.83 Å. The value found by *x*-rays for a grossularite from Mexico is 11.84, with a calculated density of 3.605 (*Strukturbericht*).

## SUMMARY

Garnets from Black Lake, Quebec, show the combination {233}, {011}, {112}. They are predominantly andradite in composition. The garnet morphology is studied in the light of the Generalized Law of Bravais. The forms observed and their relative importances conform with the space-group requirements. Conversely, the space-group is determined from the form development and the length of the cell edge can be predicted. The occasional predominance of any one form, such as {233} in the present instance, must be ascribed to influences other than that of space-group symmetry.

## REFERENCES

DANA, E. S. (1892): *System of Mineralogy*, ed. 6—New York.

DONNAY, J. D. H. (1938): Crystal space-groups determined without *x*-rays (abstract)—*Am. Mineral.*, vol. 23 (12, 2), p. 5; vol. 24, p. 184 (1939).

——— (1940): Analyse morphologique de la danburite—*Trans. Roy. Soc. Canada*, vol. 34, sec. 4, pp. 33-43.

——— and HARKER, D. (1937a): Généralisation de la loi de Bravais—*C.R.*, vol. 204, pp. 274-276.

——— (1937b): A new law of crystal morphology extending the Law of Bravais—*Am. Mineral.*, vol. 22, pp. 446-467.

——— (1940): Nouvelles tables d'extinctions pour les 230 groupes de recouvrements cristallographiques—*Naturaliste canadien*, vol. 67, pp. 33-69.

FAESSLER, CARL (1935): Quelques particularités de certains minéraux du Québec (abstract)—*Annales de l'ACFAS*, vol. 1, p. 167.

GOLDSCHMIDT, V. (1918): *Atlas der Krystallformen*, vol. 4—Heidelberg.

GROTH, P. (1908): *Chemische Krystallographie*—Leipzig.

PARSONS, A. L. (1935): Trisoctahedral garnet from West Thetford Mines, P.Q.—*Univ. Toronto Studies, Geol. Ser.*, no. 38, pp. 33-36.

POITEVIN, E. and GRAHAM, R. P. D. (1919): Etude sur la minéralogie du district de Black Lake, Québec.—*Comm. géol. Canada*, Bull. du Musée no 27, Série géol. no 35, Ottawa.

# BOULANGERITE FROM MONTGAY TOWNSHIP, ABITIBI COUNTY, QUEBEC

By J. E. HAWLEY
*Queen's University*

An interesting occurrence of the mineral, boulangerite, with associated gold and silver values, was discovered in Montgay Township, lot 6, Concession VI, Abitibi County, Quebec, in 1936. For samples of this ore and a brief description of the deposit, the writer is indebted to Mr. K. W. Fritzsche. E. C. S. Gould and G. M. Wright studied specimens of the ore at different times and some of their results are included in this paper.

L. V. Bell (1937) notes that this occurrence was known in 1933 (Bell and Bell, 1934), but not until 1936 were gold values found to accompany the mineralization. The gray mineral was identified in the field as stibnite. W. W. Longley (Ross and others, 1938) described the deposit later but made no mention of the lead minerals present.

## OCCURRENCE

The mineral discovery, made on claims held by the Alaska Development and Mineral Company, consists of a mineralized shear zone which has been traced for a length of 500 feet. It strikes N. 45° W. and dips 76° S.W.

Rocks immediately adjacent to the shearing are acidic tuffs and on either side are greenstones. The shear zone itself consists of sericite schist, heavily mineralized with pyrite and some sphalerite. A considerable amount of quartz is also present, some of which is granular while some occurs in more massive form as small lenses and narrow veinlets following the schistosity which shows much distortion.

Amphibolite dykes up to 10 feet wide also occur in the shear zone. These are only slightly mineralized according to Mr. Fritzsche, but have a concentration of nearly massive sphalerite and pyrite, 2-6 feet wide along both contacts.

The boulangerite occurs disseminated in quartz and sphalerite and as narrow, massive veinlets up to ¼ inch in width in the schist.

It is fairly abundant in several pockets about 5 feet wide and 15 feet long. Elsewhere, throughout the remaining part of the shear zone the mineral is only very sparsely disseminated.

Assays on various samples taken from this deposit show variable percentages of lead, zinc, and copper. Silver assays range from 1 to as much as 108 ounces per ton and gold from a trace to 0.61 ounces per ton.

## METALLIC MINERALS AND RELATIONS

The metallic minerals present consist of ilmenite, pyrite, arsenopyrite, chalcopyrite, sphalerite, and boulangerite, the latter containing besides minute inclusions of tetrahedrite, at least two other lead sulpho-salts, tentatively identified as plagionite and jamesonite, and one still unidentified mineral.

A study of the ore presented several interesting problems: (1) the identification of boulangerite and its distinction from meneghinite, for which almost identical etch reactions are described; (2) the nature of some of the pyrite which shows a weak anisotropism; and (3) the nature of the lead sulpho-salts present as partially replaced inclusions in the boulangerite.

## DESCRIPTIONS OF THE METALLIC MINERALS

*Ilmenite* occurs as small rounded grains in specimens of sericite schist carrying disseminated sulphides. It is locally replaced by arsenopyrite but its relation to pyrite could not be determined. It may have been derived from the sericite schist.

*Pyrite* occurs as anhedral grains and cubes up to 3/16 inch in diameter, following the schistosity in narrow bands and replacing schistose minerals. In some specimens it completely encloses minute, irregular, and curving blebs of chalcopyrite, minor sphalerite, and very fine grains of arsenopyrite, none of which appears related to any fractures. Elsewhere and even in the same specimens these same minerals border the pyrite and definitely replace it as does quartz.

In one specimen, roughly polished on linen with rolling abrasive, the pyrite was noted as being distinctly anisotropic. The same specimen was later mounted in bakelite and further polished, but was then found to be completely isotropic. Several other specimens, highly polished on lead laps, likewise appeared isotropic and the writer is not altogether certain that the heat involved in mounting in bakelite is the only factor tending to change the pyrite from the one form to the other as first noted and described by Smith (1940).

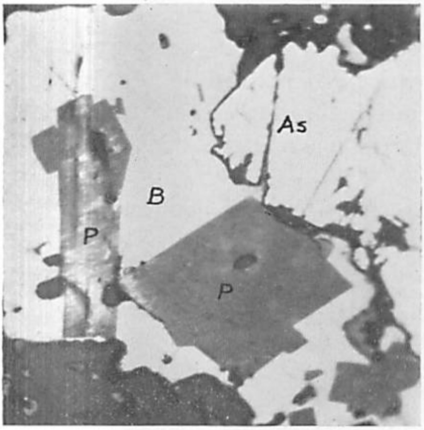
*Arsenopyrite*, chiefly in grains less than 0.1 mm. in diameter, is distributed in most pyrite-rich specimens as aggregates along the schistosity; though in places enclosed in pyrite, it is inferred to be largely later as shown by abundant replacement textures. Some overlapping in time of crystallization of the two minerals may best explain their relations. Chalcopyrite, sphalerite, and boulangerite replace the arsenopyrite slightly, but little of these or the other sulphides are in contact with it and their age relations are therefore not so certain.

Within boulangerite-sphalerite-rich specimens, however, are roughly six-sided crystals with a colour intermediate between arsenopyrite and pyrrhotite. Hardness, anisotropism, and etch reactions agree with arsenopyrite and microchemical tests gave iron, arsenic, and a doubtful test for sulphur. The only other possibility for these grains is leucopyrite which should be even whiter in colour than arsenopyrite.

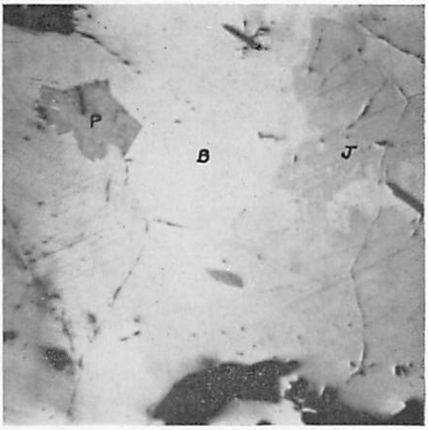
*Sphalerite with Minor Chalcopyrite and Quartz* occur together in minute stringers cutting pyrite and to a lesser extent, arsenopyrite, and are hence inferred to be contemporaneous. The sphalerite is much the more abundant and is more intimately associated with boulangerite than the pyrite and arsenopyrite. It is dark in colour, rich in iron, and entirely free from inclusions of chalcopyrite. Grains are anhedral and range from 1 to 0.1 mm. in diameter. Some are completely enclosed by boulangerite which clearly replaces it, but also, in other sections, seems to be replaced by it. Again, some overlapping in time of deposition of these two minerals may have occurred.

*Boulangerite* occurs in seams following the schistosity with widths up to ½ inch. It is light gray, fibrous, and columnar. In polished sections it is seen to occur as aggregates averaging ¼ inch in diameter; the colour is galena white; polarization colours vary from light to dark gray but are distinct. Specific gravity 5.6, hardness low (B).

In the specimens first obtained and studied the boulangerite appeared quite homogeneous. This material was largely used for a chemical analysis by Gould. A second lot obtained from Mr. Fritzsche, when polished, proved that the apparently homogeneous material when etched with either $HNO_3$ or KOH, was definitely a mixture with at least two other minerals, all apparently lead sulpho-salts, the properties of which will be given later.



*1*



*2*

FIG. 1.—Elongated, blocky, and rhombic gray grains of plagionite? (P), enclosed in white boulangerite (B); arsenopyrite (As). Etched with KOH. (×84.)

FIG. 2.—Intergrowth of blocky plagionite? (P), jamesonite? (J), and boulangerite (B). Etched with KOH. (× 84.)

Etch reactions for the boulangerite are as follows:

$HNO_3$—fumes tarnish, gradually turns black, reaction advancing as a wave, as noted for meneghinite by Short, with slow effervescence.

HCl—fumes tarnish slightly.

KCN, $FeCl_3$—negative.

KOH—negative, in some places possibly stains faint gray or brown as does specimen from San Pedro de Buena Vista, Charcas, Potosi, Bolivia.

$HgCl_2$—Faint brown colour at edge of drop, rubs clean.

Azolitmus test—stains iridescent, but washes and rubs clean.

A chemical analysis by Gould on apparently pure material from the first lot gave the following:

| | Montgay | Dana |
|---|---|---|
| Pb | 54.7 | 55.4 |
| Sb | 30.4 | 25.7 |
| S | 15.1 | 18.9 |
| | 100.2 | 100.0 |

Silver (four analyses): 0.6, 0.6, 0.5, 0 per cent.

In view of the later discovery of at least two other sulpho-salts in the boulangerite, reactions for which best fit plagionite and jamesonite, the higher antimony and lower sulphur in the above analysis compared with the theoretical amounts, may be accounted for by inclusions of these minerals.

Microchemical tests showed the following present: Pb, Zn, Fe, Ag, Sb, and Te (according to Gould), but later tests by Wright and the writer failed to check either Ag or Te, though there is no doubt about the presence of the former.

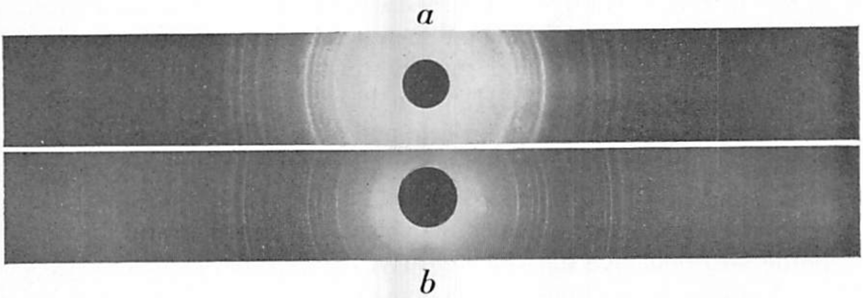


FIG. 3.—*X*-ray powder photographs with Cu-*K* radiation; camera radius $360/\pi$ mm.; *a*—boulangerite and jamesonite, Montgay Township, Quebec; *b*—boulangerite, Príbram, Bohemia (Ni filter).

Spectrographic analysis gave Fe, Pb, Zn, Ag, and Sb with traces of Ti and Se but no Bi. Both Fe and Zn may be accounted for by the presence of intimately mixed sphalerite. The Ag may be present in freibergite or tetrahedrite, which occurs as minute inclusions in the boulangerite, rather than in solid solution.

Finally, the identity of the boulangerite was established by comparison of an *x*-ray photograph made by N. W. Buerger (Fig. 1*a*) with one, kindly loaned by Professor M. A. Peacock, of boulangerite from Príbram, Bohemia (U.S. Nat. Mus. 83983) (Fig. 1*b*), whose identity was confirmed by Berry (1940). In addition to the boulangerite pattern the Montgay material shows extra lines due to intergrown jamesonite. [See Berry and Moddle, on meneghinite (this issue of these *Studies*, Fig. 3.)]

*Inclusions in Boulangerite.* At least four different minerals are present within the boulangerite as inclusions of one type or another. Of these, isotropic, gray tetrahedrite yields the characteristic etch tests. While silver was suspected in this mineral no confirmation could be obtained by microchemical tests due to the small size of the particles available. It is present in minute, rounded particles in the boulangerite—and also in what has been tentatively identified as plagionite.

*Unknown No. 1 (Plagionite ?).* The mineral plagionite(?) is barely discernible in freshly polished sections from the boulangerite, but with prolonged polishing on linen it takes on a slightly rougher surface. It is readily and immediately brought into relief by etching with standard KOH, when it changes in colour first to brown, then grayish blue, purplish, and even a deep greenish gray. It is present both as small blocky to elongated grains in some specimens, as rhombic shaped grains in others and as less regular shaped grains, on some sides of which it presents sharp angular borders to boulangerite which clearly, partly replaces it.

As the etch reactions on this mineral differ from those given by Short (1940) for plagionite, our results are included here:

Colour—grayish white, strongly anisotropic, dark bluish gray to grayish white.

Hardness—slightly greater than boulangerite.

Cleavage—prismatic.

$HNO_3$—blackens rapidly with effervescence, reaction advancing as a wave as in boulangerite. Fumes tarnish more slowly than on boulangerite.

HCl—fumes tarnish, stains darker gray.

KCN—negative.

$FeCl_3$—negative on most specimens. Some, when previously etched with KOH, turn darker brown.

KOH—immediately stains brown, then bluish gray to purplish, greenish and even iridescent.

$HgCl_2$—negative on fresh specimens; specimens previously etched with KOH turn faint brown.

Microchemical—Pb, Sb.

*Unknown No. 2 (Jamesonite ?).* This mineral occurs in small rounded grains enclosed and partly replaced by boulangerite;

colour, pale grayish blue; anisotropism, moderate dark gray to grayish white.

$HNO_3$—slowly turns brown then gray, no effervescence. Reaction much slower than on boulangerite or plagionite.

HCl—negative to slight; turns darker gray; fumes tarnish some brown.

KCN, $FeCl_3$—negative.

KOH—brownish, gray, purplish red, but reaction goes more slowly than on angular grains of plagionite.

$HgCl_2$—negative.

Aq. Reg.—fumes tarnish, stains dark black, slow effervescence.

Microchemical—Pb, Sb, but negative for Ag, Bi, Hg, As, Se. CsCl+KI give brick red precipitate.

Both colour, habit, and the slowness of the reaction with $HNO_3$ distinguish this mineral from that identified as plagionite, though the KOH reactions on both are very similar. It may be a variety of plagionite or jamesonite. The recognition of the strongest lines of the jamesonite pattern in Fig. 1*a* strengthens the identification of this mineral.

*Unknown No. 3.* The third unknown occurs always as very minute blebs and elongated lenses in boulangerite or plagionite(?). These have a pale pinkish tone, about the same hardness as boulangerite and are distinctly anisotropic, giving pinkish gray to dark gray colours. Etch reactions obtained are as follows:

$HNO_3$—negative; faint brown near contact with jamesonite(?).

HCl, KCN, $FeCl_3$, KOH, $HgCl_2$—negative.

Aq. Reg.—first turns white then slowly black and rubs gray.

No satisfactory microchemical tests have been obtained on account of the small size of the particles.

No free gold was found in any of the specimens studied.

## SUMMARY

A new occurrence of the mineral boulangerite in Montgay Township, Quebec, with associated silver and gold, is described. Two other lead sulpho-salts, tentatively identified as plagionite and jamesonite are present with it, also pyrite, arsenopyrite, sphalerite, minor chalcopyrite, and tetrahedrite. Silver may be associated with the latter or in an unidentified pinkish mineral occurring as minute blebs in boulangerite. Some of the pyrite shows distinct anisotropism which disappeared on heating when the specimen was mounted in bakelite. A suggestion is made that the method of polishing may also cause the loss of this property.

The paragenesis of the ore is as follows: ilmenite, pyrite, arsenopyrite (possibly overlapping with pyrite), quartz, sphalerite with minor chalcopyrite, lead sulpho-salts with tetrahedrite. Of the lead minerals, those identified as plagionite and jamesonite appear slightly earlier than boulangerite and are partially replaced by it.

## REFERENCES

BELL, L. V. (1937): Mining properties and development in the Rouyn-Bell River district during 1936—*Quebec Bur. Mines*, Prelim. Rep. no. 116, 85 pp.

———— and BELL, A. M. (1934): Senneterre map-area, Abitibi district—*Quebec Bur. Mines*, Ann. Rep. for 1933, pt. B, 75 pp.

BERRY, L. G. (1940): Studies of mineral sulpho-salts: III—Boulangerite and "epiboulangerite"—*Univ. Toronto Studies, Geol. Ser.*, no. 4, pp. 5-19.

ROSS, S. H., DENIS, B. T., ASBURY, W. N., LONGLEY, W. W., and AUGER, P. E. (1938): Mining properties and development work in the Abitibi and Chibougamau regions during 1937—*Quebec Bur. Mines*, Prelim. Rep. no. 120, 33 pp.

SHORT, M. N. (1940): Microscopic determination of the ore minerals—*U.S. Geol. Surv.*, Bull. 914.

SMITH, F. G. (1940): Variation in the electrical conductivity of pyrite—*Univ. Toronto Studies, Geol. Ser.*, no. 44, pp. 83-93.

# HEAT EFFECTS ON SULPHIDES AND POSSIBLE APPLICATIONS

By J. E. HAWLEY
*Queen's University*

In determining the paragenesis of an ore one is constantly reminded of the difficulty of evaluating an apparent or real difference in age between the minerals present. This is particularly true where the minerals are all of hypogene origin. That age differences may be a matter of minutes has been pointed out by metallurgists who have studied the crystallization of melts of various types, and caution has been advised in the interpretation of age relations as found in natural ores. In other cases geologists have shown that different stages of mineralization in a single deposit may be separated in time sufficiently to allow thorough solidification of the early minerals, their fracturing, and the later injection of other ore minerals. In some deposits the intrusion of various types of dyke rocks, both acidic and basic, may intervene between periods of mineralization. The time involved in these processes is necessarily largely a matter of conjecture.

In the course of investigations on iron, nickel, and copper sulphides some rather astonishing effects, produced during the heat treatment of natural sulphide specimens, seem worthy of record in the above connection, even though somewhat similar, but much more elaborate experiments were reported as long ago as 1912. Some of the experiments were made by H. F. Zurbrigg in the Mineralogical Laboratory, Queen's University, in 1933, and others by Maurice Scott in 1937.

## THE EXPERIMENTS

Polished sections, about $\frac{1}{4}$-$\frac{1}{2}$ inch in diameter, were inserted in an electric tube furnace and heated for various periods of time at different temperatures, either in air or in a current of $H_2S$. Temperatures were measured with thermocouples suitable to the temperatures involved. After cooling, which was done in the same atmosphere used in heating, the specimens were repolished and studied, proper attention being paid to the possibility that the new surfaces might not be exact replicas of the old. The results of four such experiments are described below.

*1. Development of Pyrite Veinlets in Gangue.* A specimen of Sudbury ore containing pyrrhotite with minor pentlandite in a siliceous gangue was treated at a temperature of 640° C. for two periods of two hours each in air and the evolved $SO_2$.

After heating the gangue was found to be considerably fractured, and filling the fractures were minute stringers of fine-grained pyrite. Further heat treatment yielded still more fractures and veinlets. It is apparent that volatilization of both iron and sulphur, probably from pyrrhotite, occurred to form the veinlets.

*2. Development of Pyrrhotite Veinlets in Magnetite.* A specimen of magnetite-rich ore from Sudbury containing pyrrhotite, pentlandite, and minor chalcopyrite was heated by Scott at 775° C. for eighteen hours in an atmosphere of $H_2S$.

Aside from the disappearance of both pentlandite and chalcopyrite, due undoubtedly to the formation of solid solutions, each grain of magnetite was minutely fractured, and in the fractures veinlets of anisotropic pyrrhotite were developed. It is inferred that the veinlets were the result largely of volatilization of original pyrrhotite, and any conversion of magnetite to pyrrhotite in the presence of $H_2S$ seems to have been small.

*3. Replacement of Pyrrhotite by Chalcopyrite and Formation of Veinlets of Chalcopyrite.* Specimens of mixed sulphides, pyrrhotite, chalcopyrite, sphalerite, enclosing minute blebs of chalcopyrite, and galena, with a gangue of diopside, were heated by Scott at 410° C. in a current of $H_2S$ for six hours.

The effects of the heat treatment were most pronounced on the pyrrhotite. This mineral and the diopside were minutely fractured, and in the latter small veinlets of chalcopyrite were deposited. More striking still was the fact that more than half of the pyrrhotite had been replaced by chalcopyrite with which it was in contact. The "new" chalcopyrite differed from the original in having a deeper yellow colour, but gave similar etch reactions. Many of the small blebs of chalcopyrite disappeared from within the sphalerite, but otherwise no effect was produced on it or the galena.

Further heating at 480° C. for five hours appeared to produce a still further replacement of pyrrhotite by chalcopyrite or a similar compound, and at this temperature all of the blebs of chalcopyrite had disappeared from within the sphalerite. [Buerger (1934) found unmixing and mixing of chalcopyrite in sphalerite to occur between 350° and 400° C.] Similar effects were obtained at 390° C. for six hours, but at 375° C. chalcopyrite in quartz remained unaffected.

*4. Cube Pyrite Developed in Massive Pyrrhotite.* Specimens of massive pyrrhotite from different localities were heated by Zurbrigg at a temperature of 550° C. for periods of ten to twelve hours in a current of $H_2S$. Small striated cubes of pyrite were found to develop along the exposed surfaces of the specimens with a graphic arrangement.

Schwartz (1937) in his excellent discussion of the paragenesis of pyrrhotite recalls the early work of Allen, Crenshaw and Johnston (1912) who found that pyrrhotite might be synthesized from pyrite by heating in $H_2S$ above 575° C. and that at 550° C. the reaction is readily reversible. Later Merwin and Lombard (1937, p. 217) have indicated that at 578° C. pyrrhotite and pyrite are in equilibrium at a sulphur pressure of 455 mm.

## POSSIBLE APPLICATIONS

*Development of Veinlets of Pyrite, Pyrrhotite, or Chalcopyrite.* A study of heat-treated specimens in which veinlets of either pyrite, pyrrhotite, or chalcopyrite were developed, if considered as entirely natural ore specimens, would undoubtedly lead an investigator to conclude that certain sulphides were first introduced into the host rock, that subsequent fracturing (usually attributed to deforming forces rather than heat) occurred, and that finally deposition of a later sulphide took place in the fractures so formed, the substance for which would normally be assumed to come from some mineralizing source at depth.

Without in any way implying that the above interpretation would not be the most logical and correct in the case of similar relations in natural ores, the question may be raised as to whether veinlets of pyrite, pyrrhotite, or chalcopyrite are *always* the result of direct deposition from ascending solutions or, in places, are due to volatilization of earlier formed sulphides in the presence of sulphur or hydrogen sulphide. One may also ask how certain is the usual assumption that fractures in early ore and gangue minerals are the result of forces of external origin, and how often may they be the result of heat (or cooling) such as might emanate from heat waves advancing from some intrusive below or from nearby intrusive dyke rocks, whether these are introduced during the ore forming period or some time after. Careful study of the spatial relations of the minerals in the ore deposits themselves, rather than of single laboratory specimens, with the different possibilities in mind, should enable a conclusion to be reached.

The problem of the age of the sulphide bodies at Noranda, with respect to the northerly trending diabase dyke which appears to cut them, may be recalled. On the evidence that veins of chalcopyrite with minor pyrite and pyrrhotite do break through and cross the diabase, and replace post-diabase faults, Suffel (1935) concluded that the ores are entirely post-diabase.

While not questioning Suffel's conclusion in this case the writer does wish to emphasize the fact that the common sulphides, pyrite, pyrrhotite, and chalcopyrite, may easily rearrange themselves on heating in such a way as to leave little indication that their mode of deposition was not original. This is indeed the most striking feature of the experimental results obtained.

*Replacement of Pyrrhotite by Chalcopyrite.* The usual relation of chalcopyrite to pyrrhotite, particularly in massive sulphide ores, is one of replacement of the latter by the former. Here again it is fair to assume that in detailing the paragenesis of such an ore one is inclined to note the fact, without pausing to consider the *modus operandi* of the replacement. How often is such chalcopyrite introduced in its entirety, how much by reactions between a volatile copper compound and pyrrhotite in sulphur vapour or hydrogen sulphide, and how much replacement may occur after copper has actually ceased to be added to the deposit, are questions difficult to answer though the problems should be recognized as such.

*Cube Pyrite in Massive Pyrrhotite.* The development of cube pyrite in pyrrhotite, due to heat treatment, serves chiefly as a reminder of the stability relations between these minerals in an atmosphere of sulphur, and is a function of both temperature and

$$\underset{\text{Pyrrhotite}}{\mathrm{FeS} \pm x\mathrm{S}} + \text{Sulphur} \rightleftharpoons \underset{\text{Pyrite}}{\mathrm{FeS_2}}$$

sulphur pressure. Such crystals in pyrrhotite have been noted at Sudbury and Sherritt Gordon, and at Santo Eulalia, Mexico, by Schwartz (1937).

Specimens from the latter locality are described as containing early pyrite in euhedral crystals surrounded by pyrrhotite, which is replaced by a later generation of pyrite particularly along cleavages. This latter occurrence is described as rare.

It is, however, the cube pyrite within pyrrhotite in natural ores that is so strikingly similar to that developed synthetically by heat treatment; and what should be kept in mind by the student is that the mere fact of its being surrounded by pyrrhotite does not prove its earlier age. Cube pyrite surrounded by, and necessarily replacing, schist is a case in point.

In the massive pyrite-pyrrhotite-chalcopyrite ore body at the Aldermac Mine, Quebec, are several dyke-like bodies of pyrrhotite with associated chalcopyrite cutting through almost barren pyrite. Within the pyrrhotite are scattered crystals of pyrite, in many cases striated, varying in size up to an inch or more in diameter. As far as studied, the crystals present sharp boundaries to the pyrrhotite so that no clear age relation is apparent. The early massive pyrite, it seems, reflects deposition from a medium with a sufficient sulphur content to satisfy the requirements of pyrite rather than pyrrhotite. The later pyrrhotite containing crystals of pyrite, undoubtedly reflects a decrease in sulphur in the mineralizing medium; but it is indeed difficult to ascertain whether in this case the sulphur concentration was such as to allow simultaneous crystallization of both pyrite and pyrrhotite or only sufficient for pyrrhotite which, by the still later addition of sulphur, could partially change over to pyrite. One may also ask whether the large, radiating, concretion-like masses of pyrite in such ore bodies as those of Noranda, are due to primary deposition or a later development from pyrrhotite in the presence of sulphur vapour.

## SUMMARY

Attention is called to certain effects produced in iron (nickel) and copper sulphide specimens by heat treatment in an atmosphere of air, $SO_2$, or $H_2S$. These consist chiefly of the development of stringers of pyrite, pyrrhotite, or chalcopyrite, particularly in the gangue minerals, further replacement of pyrrhotite by chalcopyrite, and the development of cube pyrite in pyrrhotite. The question is raised as to whether there are any examples of such phenomena in natural ores, due to an advancing heat wave, either coming from depth or a nearby intrusive dyke; and whether some of the relations we see in such ores are due to rearrangements occurring in iron and copper sulphides after the main introduction of these metals has ceased, but while the temperature is still high and sulphur vapour still present; or are such phenomena always to be interpreted in the usual way as purely primary. Again, caution is advised in the interpretation of the age relations of such ore minerals.

## REFERENCES

ALLEN, E. T., CRENSHAW, J. L., and JOHNSTON, J. (1912): The mineral sulphides of iron—*Am. Jour. Sci.*, vol. 33, pp. 169-236.

BUERGER, N. W. (1934): The unmixing of chalcopyrite from sphalerite—*Am. Mineral.*, vol. 19, pp. 525-530.

MERWIN, H. E. and LOMBARD, R. H. (1937): The system Cu-Fe-S—*Econ. Geol.*, vol. 32, pp. 203-241.

RAY, J. C. (1930): Synthetic sulphide replacements of ore minerals—*Econ. Geol.*, vol. 25, pp. 433-451.

SCHWARTZ, G. M. (1937): The paragenesis of pyrrhotite—*Econ. Geol.*, vol. 32, pp. 31-55.

SUFFEL, G. G. (1935): Relations of later gabbros to sulphides at the Horne Mine, Noranda, Quebec—*Econ. Geol.*, vol. 30, pp. 905-915.

# THE UNRELIABILITY OF THE HELIUM INDEX IN GEOLOGICAL CORRELATION

By N. B. Keevil
*University of Toronto*

The history of age determinations of rocks and minerals by radioactive methods is well known. Early experiments suggested a loss of helium from radioactive minerals and metamorphic rocks. However, when development of reliable analytical methods in the low concentration ranges made determinations on ordinary rocks possible, it was hoped that the minute quantities of helium formed from radioactive elements in these rocks might be retained under moderate changes in geological environment. Results on basic rocks (Urry, 1936) indicated that ages determined by the helium method were in good agreement with those obtained by the lead method as applied to radioactive minerals, and with geological data. The large error in these results discovered by the writer in cooperation with Goodman (Evans and others, 1939) proved somewhat disconcerting, but general agreement of the sequence of helium indices with geological succession still seemed to exist. The need for more fundamental research was suggested, however, by the different helium index scales found for granitic and basic rocks (1938a, 1941b) and by the evidence for escape of considerable helium from felsic minerals (1938b, 1941a).

In spite of these obvious sources of error, extensive research was continued because of the great potential value of such a method to geochronology. Some confusion has always existed in the interpretation of helium-radioactivity results because of lack of sufficient data and uncertainties in geological dating. Too often conclusions have been drawn from a single set of experiments, or conflicting data excused by the complexities of the problem—experimental errors weathering, metamorphism, grain size, geological errors, and so forth.

In order to define the limitations of the helium age method, it has been necessary to study a large number of rock specimens of all types, and to investigate a variety of minerals. Sufficient data have now been collected and the obscurity caused by the many variables has been reduced enough to allow a study of the results in their true perspective. The data summarized in the following pages show that determinations of the helium index alone cannot be used to determine geological age or sequence of ages, because of errors caused by variations in the degree of retention of helium. The helium index $I$, (1941b) is 30.65 times the ratio of the volume of helium ($10^{-5}$ cc./gm. at N.T.P.) to the rate of production of helium $a$ (ions/mg./hr.). If the experimentally determined volume represented the actual quantity of helium produced from the uranium, actino-uranium, and thorium originally trapped within the rock, the helium index would give the true helium age.

These researches have been made possible through generous donations from Mr. Hans Lundberg and the Viking Foundation. The writer is also indebted to the many who have contributed specimens and otherwise encouraged the work, to Mr. R. F. Errington for his assistance in the laboratory, and to Dr. M. A. Peacock for his recent interest in this research, and his kindness in criticizing the manuscript.

## TIME SCALE

To evaluate the usefulness of helium index determinations, it is necessary to use a time scale which is related to the geological column. The post-Cambrian and pre-Cambrian time scales assumed in the present investigation are given in Table 1. This scale was derived from what are considered to be the most reliable isotopic, radioactive, and geological data available. The greatest uncertainties are probably within the Tertiary and pre-Cambrian periods. Ages in millions of years obtained from this scale are denoted by $A$.

## SUMMARY OF RESULTS BY THE HELIUM METHOD

The results of several hundred helium index investigations on igneous rocks and minerals are summarized in Table 2. Amassing these data, more than half of which are new, required years of elaborate experimental work. Some of the values represent averages of as many as twelve age determinations involving several weeks' study. In a few cases, where marked disagreement existed between

## TABLE 1

### ASSUMED TIME SCALE IN MILLIONS OF YEARS

| POST-CAMBRIAN | | | PRE-CAMBRIAN | | |
|---|---|---|---|---|---|
| Limits | System | Average | Limits | System | Average |
| 0 | Pleistocene | 2 | 500 | | |
| | Pliocene | 10 | | | |
| 20 | Miocene | 20 | 600 | Keweenawan | |
| | Oligocene | 35 | | and | 575 |
| 40 | | | 700 | Killarnean | |
| | Eocene | 60 | | | |
| 60 | | | 800 | | |
| | Cretaceous | 72 | | | |
| 80 | | | 900 | | |
| 100 | | | 1000 | | |
| | Jurassic | 120 | | | |
| 120 | | | 1100 | Algoman | 1100 |
| 140 | | | 1200 | | |
| | Triassic | 150 | | | |
| 160 | | | 1300 | | |
| 180 | | | 1400 | | |
| | Permian | 190 | | | |
| 200 | | | 1500 | | |
| 220 | | | 1600 | | |
| 240 | | | 1700 | | |
| | Carboniferous | 250 | | | |
| 260 | | | 1800 | | |
| 280 | | | 1900 | | |
| | Devonian | 300 | | | |
| 300 | | | 2000 | | |
| 320 | | | 2100 | Keewatin | 2050 |
| | Silurian | 335 | | | |
| 340 | | | 2200 | | |
| 360 | | | 2300 | | |
| 380 | | | 2400 | | |

TABLE 1—(*Continued*)

| POST-CAMBRIAN | | | PRE-CAMBRIAN | | |
|---|---|---|---|---|---|
| Limits | System | Average | Limits | System | Average |
| | Ordovician | 380 | 2500 | | |
| 400 | | | | | |
| | | | 2600 | | |
| 420 | | | | | |
| | | | 2700 | | |
| 440 | | | | | |
| | Cambrian | 450 | | | |
| 460 | | | | | |
| 480 | | | | | |
| 500 | | | | | |

duplicate determinations, more than one value of the helium index has been included for the rock. For each sample, the helium index *I*, calculated by substituting experimental values of helium and radioactivity contents into the age equation, is compared with the probable age *A*, indicated by geological field evidence. In the last column is given the ratio of the apparent age to the expected age. For convenience the results for rocks are grouped into acidic and intermediate rocks, basic rocks, and fine-grained porphyries and lavas, and the results for minerals into magnetite, quartz, other oxides, feldspars, femic minerals, other silicates, and oxy-salts, and chlorides. In some cases the assumed age may not agree with the best geological data, and occasionally when the source was indefinite it was necessary to assume an age based upon general geological maps. In other instances, the upper and lower limits of age indicated by field relationships render the geological age subject to a wide margin of error. However, it is likely that the errors are as frequently in one direction as in the other and that the resultant effect is too small to alter the conclusions drawn in this paper.[1] The experimental errors average about 10 per cent for recent measurements, probably more for earlier determinations.

---

[1] The author invites comment on inaccuracies in geological dating, and requests correspondents to include evidence of upper and lower limits as well as indirect criteria of age.

TABLE 2

A. HELIUM INDEX AND RETENTIVITY DATA FOR ROCKS

| ROCK | LOCATION | $I$ | $A$ | $I/A$ |
|---|---|---|---|---|
| | 1. *Acidic and Intermediate Rocks* | | | |
| Granite | Castle Peak, B.C. | 56 | 65 | 0.86 |
| Syenite porphyry | Maracaibo, Venezuela (3) | 21 | 70 | 0.30 |
| Tonalite | Valverde, Calif. | 66 | 120 | 0.55 |
| Granodiorite | Grass Valley, Nev. (3) | 56 | 120 | 0.47 |
| Tonalite | Valverde, Calif. | 27 | 125 | 0.22 |
| Granodiorite | Perris, Calif. | 77 | 130 | 0.59 |
| Granite-migmatite | Chelmsford, Mass. | 68 | 220 | 0.31 |
| Granite | Fitchburg, Mass. | 43 | 220 | 0.20 |
| Granite | Quincy, Mass. | 62 | 240 | 0.26 |
| Granite-syenite | Buchans, Nfld. | 93 | 240 | 0.39 |
| Pegmatite | Ruggles, N.H. (4) | 62 | 250 | 0.25 |
| Granite | Cape Ann, Mass. | 100 | 275 | 0.36 |
| Granite | Buchans, Nfld. | 141 | 275 | 0.51 |
| Granodiorite | Dedham, Mass. (3) | 92 | 300 | 0.31 |
| Granite | Franklin, Me. | 55 | 300 | 0.18 |
| Aplite | Nipisiguit, N.B. | 41 | 300 | 0.14 |
| Granite | Hampstead, N.B. | 104 | 300 | 0.35 |
| Granite | Hanover, N.H. (4) | 37 | 330 | 0.11 |
| Gneiss | Shuswap series, B.C. | 37 | 550 | 0.07 |
| Gneissic granite | Shuswap series, B.C. | 84 | 550 | 0.15 |
| Granite | Tanganyika, S. Africa | 21 | 575 | 0.04 |
| Granite | Tanganyika, S. Africa | 185 | 575 | 0.32 |
| Granodiorite | Blue Mt., Ont. | 160 | 700 | 0.22 |
| Granite (core phase) | Taschereau, Que. | 70 | 800 | 0.08 |
| Granite (border phase) | Taschereau, Que. | 234 | 800 | 0.28 |
| Granodiorite | E. LaMotte Tp., Que. | 170 | 800 | 0.20 |
| Granite | Gananoque, Ont. | 140 | 800 | 0.17 |
| Granite | Yellowknife, N.W.T. | 125 | 800 | 0.15 |
| Granite | Flavrian Lake, Que. | 226 | 800 | 0.27 |
| Diorite | N. of Flavrian Lake, Que. | 208 | 800 | 0.25 |
| Granite | Petersen Lake, Man. | 228 | 800 | 0.27 |
| Granite | Barryfield, Ont. | 233 | 800 | 0.28 |
| Granite | Yellowknife, N.W.T. | 371 | 900 | 0.41 |
| Aplogneiss | Tanganyika, S. Africa | 21 | 1200 | 0.02 |
| Granodiorite | Tanganyika, S. Africa | 240 | 1200 | 0.18 |
| Hornblende gneiss | Kimberley, S. Africa (2) | 263 | 1200 | 0.20 |
| Granodiorite | Varsan Tp., Que. | 945 | 1300 | 0.66 |
| Litchfieldite | Blue Mt., Ont. | 800 | 1500 | 0.48 |

TABLE 2—A (*Continued*)

| ROCK | LOCATION | *I* | *A* | *I/A* |
|---|---|---|---|---|
| Gneiss | Franklin, N.J. | 113 | 1500 | 0.07 |
| Diorite | Red Lake, Ont. | 130 | 1700 | 0.07 |

2. *Basic Rocks*

| ROCK | LOCATION | *I* | *A* | *I/A* |
|---|---|---|---|---|
| Basalt | Steens Mt., Ore. (3) | 6.7 | 10 | 0.67 |
| Basalt | Douglas Creek, Wash. (3) | 7.8 | 15 | 0.52 |
| Basalt | Tower Falls, Wyo. (4) | 5.5 | 15 | 0.37 |
| Basalt | Overhanging Cliff, Yellowstone Park | 11 | 20 | 0.55 |
| Basalt | Picture Gorge, Wash. (3) | 9.1 | 20 | 0.45 |
| Felsite | Mt. Pawagarh, India (1) | 5 | 20 | 0.25 |
| Tholeiite (Cleveland dike) | Bolam Co., Durham, England (1)(4) | 17 | 30 | 0.57 |
| Basalt | Crescent Hill, Yellowstone Park (4). | 9 | 30 | 0.30 |
| Basalt | Lower Silesia, Germany (3) | 17 | 35 | 0.48 |
| Basalt | Giant's Causeway, Ireland (4) | 22 | 40 | 0.55 |
| Deccan basalt | Mt. Pawagarh, India (1) | 37 | 60 | 0.62 |
| Basalt | Geode Creek, Yellowstone Park (4) | 36 | 60 | 0.60 |
| Basic dike | Little Hatchet Mts., New Mexico (3) | 47 | 70 | 0.67 |
| Kimberlite | Kimberley, S. Africa (2) | 57 | 70 | 0.81 |
| Olivine melilitite | Kimberley, S. Africa (2) | 49 | 70 | 0.70 |
| Lherzolite | Kimberley, S. Africa (2) | 22 | 70 | 0.31 |
| Harzburgite | Kimberley, S. Africa (2) | 12 | 70 | 0.17 |
| Saxonite | Kimberley, S. Africa (2) | 13 | 70 | 0.19 |
| Basic rock | Little Hatchet Mts., New Mexico (3) | 30 | 100 | 0.30 |
| Porphyrite | California (3) | 54 | 120 | 0.45 |
| Basic autolith | New Mexico (3) | 56 | 120 | 0.47 |
| Lamprophyre | Eustis Mine, Que. | 52 | 130 | 0.40 |
| Diabase | Buchans, Nfld. | 59 | 130 | 0.45 |
| Diabase | Little Hatchet Mts., New Mexico (3) | 80 | 150 | 0.53 |
| Diabase | N. Star Mine, Calif. (3) | 77 | 150 | 0.51 |
| Diabase | Virginia (5) | 95 | 150 | 0.63 |
| Diabase | New Haven, Conn. (3) | 79 | 150 | 0.52 |
| Trap rock | Cape Spencer, N.S. (3) | 87 | 150 | 0.58 |
| Diabase | Palisades, N.Y. | 81 | 150 | 0.54 |
| Basalt | Mt. Clifton, N.Y. (3) | 88 | 150 | 0.59 |
| Basalt | Oldwick, N.J. (4) | 59 | 150 | 0.39 |
| Basalt | Watchung, N.J. | 47 | 150 | 0.31 |
| Camptonite | Burlington, Vt. (3) | 84 | 150 | 0.56 |
| Diabase | Lewiston, Me. (3) | 73 | 150 | 0.48 |
| Tinguaite | Monteregian Hills, Que. (3) | 26 | 150 | 0.17 |
| Lamprophyre | Eustis Mine, Que. | 77 | 180 | 0.43 |
| Diabase | Buchans, Nfld. | 60 | 180 | 0.33 |

TABLE 2—A (*Continued*)

| ROCK | LOCATION | *I* | *A* | *I/A* |
|---|---|---|---|---|
| Basic rock | Bukkas Mts., Hungary (3) | 21 | 190 | 0.11 |
| Basic rock | Brighton, Mass. (3) | 133 | 250 | 0.53 |
| Monchiquite | Riasg Buidhe, Scotland | 109 | 250 | 0.44 |
| Monchiquite | Kilchattan, Scotland | 80 | 250 | 0.32 |
| Gabbro | Carrock Fells, England (3) | 224 | 250 | 0.89 |
| Basalt | Perth, Scotland (3) | 118 | 250 | 0.47 |
| Basalt | Shropshire, England (3) | 118 | 250 | 0.47 |
| Basalt | Titterstone Clee, England (3) | 112 | 250 | 0.45 |
| Dolerite | Westmoreland, England (3) | 196 | 250 | 0.78 |
| Camptonite | Franklin, N.J. | 150 | 250 | 0.60 |
| Basic rock | St. George, N.B. | 94 | 300 | 0.31 |
| Basic rock | Mt. Orford, Que. (3) | 90 | 300 | 0.30 |
| Trap dike | Chapel Pond, N.Y. (3) | 135 | 300 | 0.45 |
| Amphibolite | Buchans, Nfld. | 332 | 330 | 1.01 |
| Diabase | Bunker Hill, Penn. (3) | 191 | 350 | 0.55 |
| Basalt | Bunker Hill, Penn. (3) | 68 | 360 | 0.19 |
| Trap rock | Stark's Knob, N.Y. (3) | 136 | 380 | 0.36 |
| Basalt | Unicoi formation, Tenn. (3) | 178 | 450 | 0.39 |
| Basic dike | Beltian Series, South B.C. (3) | 200 | 550 | 0.36 |
| Diabase dike | Long Lake, Wyo. | 226 | 575 | 0.38 |
| Diabase dike | Noranda, Que. | 242 | 575 | 0.40 |
| Trap rocks | Champion Mine, Mich. (3) | 261 | 575 | 0.44 |
| Trap rocks | Atlanta Mine, Mich. (3) | 182 | 575 | 0.32 |
| Trap rocks | Calumet and Hecla Mine, Mich. (3) | 248 | 575 | 0.43 |
| Ophite | Calumet and Hecla Mine, Mich. (3) | 255 | 575 | 0.43 |
| Trap rock | Quincy Mine, Mich. (3) | 240<br>985<br>812 | 575 | 0.40<br>1.64<br>1.35 |
| Trap rock | Ahmeek Mine, Mich. (3) | 305 | 575 | 0.51 |
| Trap rock | Owl Creek, Mich. (3) | 161 | 575 | 0.27 |
| Greenstone | N. Cliff Mine, Mich. (3) | 230 | 575 | 0.38 |
| Basic flow | Phoenix Mine, Mich. (3) | 162 | 575 | 0.27 |
| Trap rock | Bear Tooth Range, Wyo. (4) | 1050 | 575 | 1.75 |
| Basic dike | Bear Tooth Range, Wyo. (4) | 241 | 575 | 0.42 |
| Norite | Worthington, Ont. (3) | 267<br>94 | 575 | 0.45<br>0.16 |
| Diabase | Ropruchei, Russia | 600 | 575 | 1.00 |
| Diabase | Yellowknife, N.W.T. | 1160 | 575 | 1.93 |
| Diabase | Gogebic Range, Wis. | 190<br>320(3) | 600 | 0.30<br>0.53 |
| Gabbro | Woollen Mill, N.Y. (3) | 472 | 600 | 0.75 |
| Diabase | Great Bear Lake, N.W.T. (3) | 485 | 600 | 0.77 |

TABLE 2—A (*Continued*)

| ROCK | LOCATION | *I* | *A* | *I/A* |
|---|---|---|---|---|
| Basalt | Gwalior Series, India (1) | 500 | 600 | 0.80 |
| Dolerite | Morar group, India (1) | 296 | 600 | 0.47 |
| Basic dike | Red Lake, Ont. | 131 | 1200 | 0.10 |
| Basic appinite | Kimberley, S. Africa (2) | 325 | 1200 | 0.25 |
| Appinite | Kimberley, S. Africa (2) | 97 | 1200 | 0.07 |
| Granulite | Kimberley, S. Africa (2) | 16 | 1200 | 0.01 |
| Norite | Stillwater Complex, Wyo. | 1920 | 1200 | 1.48 |
| Eclogite | Kimberley, S. Africa (2) | 235 | 1200 | 0.18 |
| Pillow lava | Huron Claim, Man. | 1840 | 2200 | 0.71 |
| | 3. *Fine-Grained Porphyries and Lavas* | | | |
| Porphyritic basalt | Yellowstone Park, Wyo. (4) | 5 | 35 | 0.14 |
| Obsidian | Yellowstone Park, Wyo. (4) | 8 | 35 | 0.23 |
| Rhyolite | Yellowstone Park, Wyo. (4) | 22 | 40 | 0.55 |
| Felsite | Mt. Pawagarh, India (1) | 5 | 60 | 0.08 |
| Basalt | N. Attleboro, Mass. | 22 | 230 | 0.09 |
| Rhyolite | N. Attleboro, Mass. | 47 | 230 | 0.20 |
| Porphyry-rhyolite | Buchans, Nfld. | 31 | 300 | 0.10 |
| Quartz porphyry | Buchans, Nfld. | 21 | 300 | 0.07 |
| Feldspar porphyry | Buchans, Nfld. | 39 | 300 | 0.13 |
| Felsite | Lynn, Mass. (3) | 36 | 300 | 0.12 |
| Andesite | Dalhousie Mt., N.S. (3) | 160 | 300 | 0.48 |
| Grey tuff | Rowley, Mass. (3) | 152 | 320 | 0.47 |
| Trachyte | Buchans, Nfld. | 21 | 350 | 0.06 |
| Lava | Buchans, Nfld. | 26 | 350 | 0.07 |
| Lava-breccia | Buchans, Nfld. | 56 | 350 | 0.16 |
| Dacite | Buchans, Nfld. | 9 | 350 | 0.03 |
| Amygdaloidal lava | Mosedale, England | 26 | 380 | 0.07 |
| Basic lava | Keswick, England | 15 | 380 | 0.04 |
| Stockdale rhyolite | Westmoreland, England | 5 | 380 | 0.01 |
| Hornblende schist | Beartooth Range, Wyo. (4) | 46 | 550 | 0.08 |
| Felsite | Tamarack Mine, Mich. (4) | 20 | 575 | 0.03 |
| Quartz porphyry | Pearl Lake, Ont. | 1164 | 1000 | 1.08 |
| Porphyry | Millerton, Hollinger Gold Mines, Ont. | 693 | 1000 | 0.65 |
| Porphyry | Acme Gold Mines, Ont. | 188 | 1000 | 0.18 |
| Porphyry | Bristol Tp., Ont. | 117 | 1000 | 0.11 |
| Quartz porphyry | Joliet, Noranda, Que. | 133 | 1000 | 0.12 |
| Porphyry | Dome Gold Mines, Ont. | 40 | 1000 | 0.04 |
| Porphyry | S.E. of Pearl Lake, Ont. | 56 | 1000 | 0.05 |
| Porphyry | Preston East Dome, Ont. | 59 | 1000 | 0.06 |
| Porphyry pebble | Dome Gold Mines, Ont. | 134 | 1200 | 0.10 |
| Quartz porphyry | Red Lake, Ont. | 49 | 1450 | 0.03 |

## TABLE 2

### B. HELIUM INDEX AND RETENTIVITY DATA FOR MINERALS

| TYPE OF SPECIMEN | SOURCE | LOCATION | *I* | *A* | *I/A* |
|---|---|---|---|---|---|
| | | 1. *Feldspar* | | | |
| Feldspar | Riverside granodiorite | Valverde, Calif. | 55 | 120 | 0.46 |
| Feldspar | Bonsall tonalite | Valverde, Calif. | 18 | 125 | 0.14 |
| Plagioclase | Lakeview tonalite | Perris, Calif. | 41 | 135 | 0.30 |
| Feldspar | Diabase | Palisades, N.Y. (5) | 36 | 140 | 0.26 |
| Feldspar | Diabase | W. Virginia (5) | 35 | 140 | 0.25 |
| Plagioclase | Diabase | Gilboa Quarry, Delaware R. | 92 | 150 | 0.61 |
| Feldspar and trace biotite | Pegmatite | Chelmsford, Mass. | 19 | 220 | 0.09 |
| Feldspar and trace biotite | Pegmatite | Fitchburg, Mass. | 19 | 220 | 0.09 |
| Feldspar and quartz | Pink granite | Buchans, Nfld. | 22 | 240 | 0.09 |
| Plagioclase | Alkali granite | Quincy, Mass. | 49 | 240 | 0.20 |
| Microperthite | Alkali granite | Cape Ann, Mass. | 64 | 275 | 0.23 |
| Plagioclase | Diabase | Yellowknife, N.W.T. | 101 | 575 | 0.17 |
| Plagioclase | Sekukuni norite | Bushveld Complex, Africa | 70 | 575 | 0.12 |
| Pink feldspar | Rapakivi granite | Finland | 279 | 575 | 0.47 |
| Green feldspar | Rapakivi granite | Finland | 39 | 575 | 0.07 |
| Amazonite | Pegmatite | Franklin, N.J. | 13 | 600 | 0.02 |
| Plagioclase | Pegmatite | Franklin, N.J. | 153 | 600 | 0.25 |
| Albite and microcline | Syenodiorite | Blue Mt., Ont. | 137 | 700 | 0.19 |
| Labradorite | Anorthite deposit | Adirondacks, N.Y. | 101 | 750 | 0.13 |
| Feldspar with quartz | Pink granite | Barryfield, Ont. | 195 | 800 | 0.23 |
| Feldspar with quartz | Pink granite | Petersen Lake, Man. | 13 | 800 | 0.02 |
| Pink feldspar | Granite | Gananoque, Ont. | 4300 | 800 | 5.4 |
| Feldspar | Granite | Yellowknife, N.W.T. | 158 | 900 | 0.17 |
| Feldspar | Granite | Finland | 36 | 900 | 0.04 |

TABLE 2—B (*Continued*)

| TYPE OF SPECIMEN | SOURCE | LOCATION | *I* | *A* | *I/A* |
|---|---|---|---|---|---|
| Feldspar | Granite | Yellowknife, N.W.T. | 89 | 900 | 0.10 |
| Feldspar | Granite | Flavrian Lake, Que. | 171 | 1000 | 0.16 |
| Plagioclase | Pillow lava | Huron Claim, Man. | 1175 | 2200 | 0.45 |
| 2. *Femic Minerals* | | | | | |
| Chrome diopside | Inclusion | Kimberley, S.A. (2) | 18 | 100 | 0.18 |
| Pyroxene | Diabase | Palisades, N.Y. (5) | 103 | 140 | 0.73 |
| Pyroxene | Diabase | W. Virginia (5) | 102 | 140 | 0.73 |
| Riebeckite and aegerite | Alkali granite | Quincy, Mass. | 86 | 240 | 0.36 |
| Bronzite | Malips drift bronzitite | Bushveld Complex, Africa | 742 | 575 | 1.23 |
| Augite | Sekukuni norite | Bushveld Complex, Africa | 588 | 575 | 0.96 |
| Hypersthene | Sekukuni norite | Bushveld Complex, Africa | 551 | 575 | 0.92 |
| Pyroxene | Diabase | Yellowknife, N.W.T. | 1310 | 575 | 2.19 |
| Olivine | Diabase | Yellowknife, N.W.T. | 1225 | 575 | 2.05 |
| Hedenbergite | Separated from magnetite | Port Henry, N.Y. | 127 | 600 | 0.20 |
| Pyroxene and hornblende | Pyroxenite | Red Lake, Ont. | 988 | 1310 | 0.70 |
| Augite and femics | Diabase | Gilboa Quarry, Delaware R. | 182 | 150 | 1.21 |
| Hornblende | Lakeview tonalite | Perris, Calif. | 200 | 135 | 1.48 |
| Hornblende | Amphibolite | Buchans, Nfld. | 332 | 330 | 1.01 |
| Hornblende | Granite | Finland | 264 | 900 | 0.27 |
| Hornblende | Granite | Flavrian Lake, Que. | 193 | 1000 | 0.18 |
| Hornblende | Coarse basic dyke | Red Lake, Ont. | 5450 | 1300 | 3.84 |
| Tremolite | Separated from magnetite | Moose Mt., Ont. | 1550 | 1800 | 0.76 |
| Hornblende | Pillow lava | Huron Claim, Man. | 3030 | 2200 | 1.18 |
| Hornblende and chlorite | Granite | Red Lake, Ont. | 315 | 1300 | 0.22 |
| Hornblende and chlorite | Granite | Red Lake, Ont. | 498 | 1300 | 0.35 |

TABLE 2—B (*Continued*)

| TYPE OF SPECIMEN | SOURCE | LOCATION | *I* | *A* | *I/A* |
|---|---|---|---|---|---|
| Hornblende and chlorite | Diorite | Red Lake, Ont. | 78 | 1320 | 0.05 |
| Hornblende and chlorite | Diorite | Red Lake, Ont. | 1060 | 1320 | 0.74 |
| Phlogopite | Inclusion | Kimberley, S.A. (2) | 13 | 100 | 0.13 |
| Biotite | Riverside granodiorite | Valverde, Calif. | 52 | 120 | 0.43 |
| Biotite | Bonsall tonalite | Valverde, Calif. | 150 | 125 | 1.2 |
| Biotite | Lakeview tonalite | Perris, Calif. | 91 | 135 | 0.67 |
| Biotite | Alkaline granite | Cape Ann, Mass. | 183 | 275 | 0.67 |
| Biotite | Rapakivi granite | Finland | 125 | 575 | 0.21 |
| Brown mica | With cyprene | Franklin, N.J. | 520 | 600 | 0.83 |
| Biotite | Syenodiorite | Blue Mt., Ont. | 215 | 700 | 0.29 |
| Hornblende and biotite | Grey granite | Buchans, Nfld. | 297 | 275 | 1.08 |
| Ferromagnesians | Basic rock | St. George, N.B. | $<70$ | 300 | $<0.23$ |
| Ferromagnesians | Diabase | Ropruchei, Russia | 1080 | 575 | 1.80 |
| Hornblende and biotite | Granite | Yellowknife, N.W.T. | 272 | 900 | 0.29 |
| Hornblende and biotite | Granite | Yellowknife, N.W.T. | 594 | 900 | 0.62 |
| Hornblende concentrate | Basic dyke | Red Lake, Ont. | 243 | 1300 | 0.17 |
| Hornblende concentrate | Basic dyke | Red Lake, Ont. | 530 | 1300 | 0.37 |
| Femic concentrate | Quartz porphyry | S.E. of Pearl Lake, Ont. | 172 | 1000 | 0.16 |
| Femic concentrate | Quartz porphyry | Red Lake, Ont. | 56 | 1450 | 0.04 |
| Femic concentrate | Diorite | Red Lake, Ont. | 206 | 1700 | 0.11 |
| 3. *Silicates* | | | | | |
| Sphene | Volcanic rock | Laacher See (6) | .12 | 2 | 0.061 |
| Zircon | Volcanic rock | Monte Somma, Italy (6) | 0.1 | 2 | 0.05 |
| Zircon | Volcanic rock | Mayen Eifel, Germany (6) | 0.9 | 2 | 0.45 |
| Zircon | Volcanic rock | Campbell Is., N.Z. (6) | 1.6 | 10 | 0.16 |
| Zircon | Volcanic rock | Expailly, Fr. (6) | 5.6 | 20 | 0.28 |
| Zircon | Volcanic rock | N.E. Tasmania (6) | 38 | 120 | 0.31 |

TABLE 2—B (*Continued*)

| TYPE OF SPECIMEN | SOURCE | LOCATION | *I* | *A* | *I/A* |
|---|---|---|---|---|---|
| Garnet | Corroded inclusion | Kimberley, S.A. (2) | 21 | 100 | 0.21 |
| Zircon | Xenocrysts in Kimberlite | Kimberley, S.A. (2) | 30 | 100 | 0.30 |
| Garnet | Wards minerals | Fort Wrangel, Alaska | 130 | 130 | 1.00 |
| Garnet | Wards minerals | Fort Wrangel, Alaska | 57 | 130 | 0.44 |
| Garnet | Wards minerals | Fort Wrangel, Alaska | 350 | 130 | 2.70 |
| Zircon | Lakeview tonalite | Perris, Calif. | 23 | 135 | 0.17 |
| Sphene | Lakeview tonalite | Perris, Calif. | 30 | 135 | 0.22 |
| Garnet | Wards minerals | Hot Springs, Ark. | 246 | 250 | 0.99 |
| Beryl | | Mass., U.S.A. (6) | 1532 | 300 | 5.1 |
| Datolite | Mine dump | Owl Creek, Mich. (3) | 255 | 575 | 0.44 |
| Prehnite | Mine dump | Ahmeek, Mich. (3) | 120 | 575 | 0.20 |
| Willemite | Massive willemite | Franklin, N.J. | 118 | 600 | 0.19 |
| Willemite | With franklinite ore | Sterling Hill, N.J. | 224 | 600 | 0.36 |
| Willemite | Massive willemite | Sterling Hill, N.J. | 250 | 600 | 0.40 |
| Barysilite | Mixed sample | Franklin, N.J. | 77 | 600 | 0.12 |
| Fowlerite | Separated from calcite and franklinite | Franklin, N.J. | 225 | 600 | 0.36 |
| Fowlerite | Separated from zincite | Sterling Hill, N.J. | 438 | 600 | 0.70 |
| Calcium larsenite | Impure sample | Franklin, N.J. | 185 | 600 | 0.30 |
| Roepperite | Massive roepperite | Sterling Hill, N.J. | 241 | 600 | 0.39 |
| Hancockite | With franklinite | Franklin, N.J. | 106 | 600 | 0.17 |
| Friedelite | Pure mineral, fine grain | Sterling Hill, N.J. | 95 | 600 | 0.15 |
| Schefferite | Pure crystal | Franklin, N.J. | 2270 | 600 | 3.63 |
| Garnet | Part of good crystal | Franklin, N.J. | 191 | 600 | 0.31 |
| Vesuvianite | Separated from friedelite | Franklin, N.J. | 343 | 600 | 0.55 |

TABLE 2—B (*Continued*)

| TYPE OF SPECIMEN | SOURCE | LOCATION | *I* | *A* | *I/A* |
|---|---|---|---|---|---|
| Zircon | Active mineral | Ilmen Mts., Urals (6) | 164 | 200 | 0.82 |
| Zircon | Active mineral | Cheyenne, Col. (6) | 122 | 230 | 0.53 |
| Zircon | Active mineral | Green River, N.C. (6) | 125 | 230 | 0.54 |
| Zircon | Active mineral | Brevik Langesundfjord, Norway (6) | 45.6 | 300 | 0.15 |
| Beryl | Active mineral | Chester, Pa., U.S.A. (6) | 150 | 300 | 0.50 |
| Beryl | Active mineral | Acworth, N.H. (6) | 89000 | 300 | 297 |
| Zircon | Active gem gravels—brown | Ceylon (6) | 211 | 600 | 0.35 |
| Zircon | Active gem gravels—white | Ceylon (6) | 69 | 600 | 0.11 |
| Zircon | Active mineral | Sebastapol, Renfrew, Ont. (6) | 547 | 1000 | 0.51 |
| Beryl | Active mineral | Arendal, Norway (6) | 160 | 1000 | 0.15 |
| Titanite | Active mineral | Cold Spring, N.Y. (6) | 342 | 1000 | 0.32 |
| Titanite | Active mineral | Lewis Co., N.Y. (6) | 452 | 1000 | 0.42 |
| Titanite | Active mineral | Renfrew Co., Ont. (6) | 196 | 1000 | 0.18 |
| Titanite | Active mineral | Renfrew Co., Ont. (6) | 593 | 1000 | 0.55 |
| Titanite | Active mineral | Twedestrand, Norway (6) | 170 | 1000 | 0.16 |
| Titanite | Active mineral | Twedestrand, Norway (6) | 400 | 1000 | 0.37 |
| Titanite | Active mineral | Arendal, Norway (6) | 343 | 1000 | 0.32 |
| Zircon | Xenolith (active) | Kimberley, S.A. (6) | 288 | 1200 | 0.22 |
| 4. *Quartz* | | | | | |
| Quartz | Riverside granodiorite | Valverde, Calif. | 40 | 120 | 0.33 |
| Quartz | Lakeview tonalite | Perris, Calif. | 74 | 135 | 0.55 |
| Quartz | Alkali granite | Quincy, Mass. | 86 | 240 | 0.36 |
| Quartz | Harvard collection | Arkansas | 145 | 250 | 0.58 |
| Quartz | Alkali granite | Cape Ann, Mass. | 102 | 275 | 0.37 |
| Quartz | Grey granite | Buchans, Nfld. | 111 | 275 | 0.40 |

TABLE 2—B (*Continued*)

| TYPE OF SPECIMEN | SOURCE | LOCATION | *I* | *A* | *I/A* |
|---|---|---|---|---|---|
| Quartz | Rapakivi granite | Finland | 30 | 575 | 0.05 |
| Quartz | Granite | Yellowknife, N.W.T. | 147 | 900 | 0.15 |
| Quartz | Gold ore | Dome Mines, Ont. | 3720 | 1000 | 3.47 |
| Quartz | Vein quartz | Bristol Tp., Ont. | 1304 | 1000 | 1.22 |
| Quartz | Quartz porphyry | S.E. of Pearl Lake, Ont. | 40 | 1000 | 0.04 |
| Quartz | Quartz porphyry | Preston East Dome, Ont. | 69 | 1000 | 0.06 |
| Quartz | Granite | Flavrian Lake, Que. | 95 | 1000 | 0.09 |
| Quartz | Granite | Tanganyika, S.A. | 41 | 1000 | 0.04 |
| 5. *Magnetite* | | | | | |
| Magnetite | Ore, partly oxidized | Chu Chua, B.C. | 23 | 35 | 0.67 |
| Magnetite | Ore | Great Western Mine, Utah (5) | 26 | 35 | 0.74 |
| Magnetite | Ore | Black Magnetic Mine, Utah (5) | 37 | 35 | 1.06 |
| Magnetite | Foliated magnetite and calcite | Mémé, T.N., Haiti (5) | 60 | 60 | 1.00 |
| Magnetite | Ore | Fierro, New Mexico (5) | 60 | 60 | 1.00 |
| Magnetite | Copper ore | Prince of Wales Island, Alaska (5) | 82 | 90 | 0.91 |
| Magnetite | Ore | Lynn Valley, B.C. (5) | 81 | 90 | 0.90 |
| Magnetite | Contact deposits | Texada Is., B.C. (5) | 129 | 100 | 1.29 |
| Magnetite | Ore | Cornwall, Pa. (5) | 195 | 140 | 1.39 |
| Magnetite | Basic pegmatite | Goose Creek, W. Va. (5) | 275 | 140 | 1.96 |
| Magnetite | Ore | Boyertown, Pa. (5) | 179 | 140 | 1.28 |
| Magnetite | Ore | French Creek, Pa. (5) | 270 | 140 | 1.93 |
| Magnetite | Magnetite-quartz vein | Gerrish Mt., N.S. (5) | 128 | 140 | 0.91 |
| Magnetite | Crystals | Digby Neck, N.S. | 282 | 140 | 2.01 |
| Magnetite | Associated Triassic flow | Lakeville, N.S. (5) | 181 | 140 | 1.29 |

TABLE 2—B (*Continued*)

| TYPE OF SPECIMEN | SOURCE | LOCATION | *I* | *A* | *I/A* |
|---|---|---|---|---|---|
| Magnetite | Massive magnetite | Magnetite Cove, Ark. | 42 | 150 | 0.28 |
| Magnetite | Ore slightly oxidized | Magnitnaya, Urals (5) | 303 | 250 | 1.21 |
| Magnetite | Ore + gangue | Vyssokaya, Urals (5) | 316 | 300 | 1.05 |
| Magnetite | Ore + gangue | Blagodat, Urals (5) | 385 | 300 | 1.28 |
| Magnetite | Diabase | Yellowknife, N.W.T. | 7350 | 575 | 12.25 |
| Titanomagnetite | Magnet heights felsic, magnetite rock | Bushveld Complex, Africa | 39200 | 575 | 6.53 |
| Titanomagnetite | Fine grained magnetite and greenish gangue | Hart Tp., Ont. (5) | 1150 | 600 | 1.84 |
| Magnetite | U. of T. collection | Port Henry, N.Y. | 230 | 600 | 0.37 |
| Magnetite | Magnetite sample | Franklin, N.J. | 181 | 600 | 0.29 |
| Magnetite | Fine-grained magnetite and apatite | Kiruna, Sweden (5) | 1225 | 1000 | 1.14 |
| Titanomagnetite | Titaniferous magnetite | Lake St. John, Que. | 1100 | 1000 | 1.03 |
| Titanomagnetite | U. of T. collection | Moose Mt., Ont. | 546 | 1800 | 0.27 |
| Titanomagnetite | Pillow lava | Huron Claim, Man. | >60 | 2200 | >0.02 |
| | | 6. *Other Oxides* | | | |
| Hematite | Pisolitic hematite | Antrim, Ireland (6) | 7 | 50 | 0.14 |
| Hematite | Hematite | Antrim, Ireland (6) | 25 | 50 | 0.50 |
| Hematite | Spathic ore | Kittering, England (6) | 13 | 120 | 0.11 |
| Hematite | Oolitic ore | Wurtemburg, Germany (6) | 33 | 120 | 0.27 |
| Hematite | Spathic ore | Cleveland, England (6) | 8 | 120 | 0.07 |
| Hematite | Hematite | Cumberland, England (6) | 126 | 250 | 0.50 |
| Limonite | Limonite | Forest of Dean, England (6) | 13 | 250 | 0.05 |

TABLE 2—B (*Continued*)

| TYPE OF SPECIMEN | SOURCE | LOCATION | *I* | *A* | *I/A* |
|---|---|---|---|---|---|
| Hematite | | Caen, France (6) | 119 | 300 | 0.40 |
| Chromite | Dwars River chromitite | Bushveld Complex, Africa | 65 | 575 | 0.11 |
| Franklinite | Mixed ore | Franklin, N.J. | 174 | 600 | 0.28 |
| Franklinite | Mixed ore | Sterling Hill, N.J. | 197 | 600 | 0.32 |
| Franklinite | Separated from calcite and fowlerite | Franklin, N.J. | 216 | 600 | 0.35 |
| Franklinite | Separated from calcite | Franklin, N.J. | 369 | 600 | 0.59 |
| Zincite | Separated from fowlerite | Sterling Hill, N.J. | 153 | 600 | 0.25 |
| Pitchblende | Radioactive mineral | Colorado (2) | 3.8 | 60 | 0.06 |
| Ishikawaite | Radioactive mineral | Ishikawa, Japan (7) | 71 | 120 | 0.59 |
| Samarskite | Radioactive mineral | Ishikawa, Japan (7) | 80 | 120 | 0.67 |
| Fergusonite | Radioactive mineral | Naigi, Japan (7) | 38 | 120 | 0.31 |
| Pitchblende | Radioactive mineral | Joachimsthal, Africa (6) | 1.4 | 230 | 0.01 |
| Pitchblende | Radioactive mineral | Cornwall, England (6) | 4.7 | 230 | 0.02 |
| Pitchblende | Radioactive mineral | Katanga, Africa (8) | 9.6 | 600 | 0.02 |
| Thorianite | Radioactive mineral | Ceylon (6) | 242 | 600 | 0.39 |
| Euxenite | Radioactive mineral | Saetersdalen, Norway (9) | 236 | 1000 | 0.22 |
| 7. *Carbonates, Phosphates, Sulphates, Halides, and Borates* | | | | | |
| Sphaerosiderite | | Niederplies, Germany (6) | 7.2 | 35 | 0.20 |
| Calcite | Porphyry | Buchans, Nfld. | 11 | 300 | 0.03 |
| Calcite | Amygdule in lode | Champion Mine, Mich. (3) | 184 | 575 | 0.31 |
| Calcite | Amygdule in lode | Champion Mine, Mich. (3) | 244 | 575 | 0.41 |
| Calcite | Amygdule in lode | Champion Mine, Mich. (3) | 1540 | 575 | 2.57 |
| Calcite | Crystal | Franklin, N.J. | 198 | 600 | 0.32 |

TABLE 2—B (*Continued*)

| TYPE OF SPECIMEN | SOURCE | LOCATION | *I* | *A* | *I/A* |
|---|---|---|---|---|---|
| Calcite | Crystal aggregate | Sterling Hill, N.J. | 615 | 600 | 0.98 |
| Calcite | Separated from franklinite and fowlerite | Franklin, N.J. | 2390 | 600 | 3.82 |
| Calcite | Crystal | Sterling Hill, N.J. | 10400 | 600 | 16.6 |
| Calcite | Separated from franklinite | Franklin, N.J. | 15400 | 600 | 24.6 |
| Siderite with iron olivine | Separated from magnetite | Franklin, N.J. | 283 | 600 | 0.45 |
| Monazite | Radioactive mineral | Ishikawa, Japan (7) | 71 | 120 | 0.59 |
| Monazite | Radioactive mineral | Korea (7) | 53 | 120 | 0.44 |
| Monazite | Radioactive mineral | Ishikawa, Japan (7) (9) | 62 | 120 | 0.52 |
| Apatite | Lakeview tonalite | Perris, Calif. | 43 | 135 | 0.32 |
| Apatite | Separated from garnet | Franklin, N.J. | 321 | 600 | 0.51 |
| Anhydrite | Oil-well | Lake Co., Fla. (3) | 23 | 70 | 0.33 |
| Barite | Ore-body | Buchans, Nfld. | 80 | 150 | 0.53 |
| Barite | Mine | Calumet and Hecla, Mich. (3) | 266 | 575 | 0.44 |
| Barite | Impure massive | Franklin, N.J. | 1140 | 600 | 1.83 |
| Fluorite | Active mineral | Ivigtut, Greenland | 236 | 1000 | 0.22 |
| Sussexite | Centre of banded specimen | Franklin, N.J. | 3500 | 600 | 5.60 |

Many of the values represent averages of several determinations (two to twelve). Except for those denoted by the following numbers, the determinations were made by the writer and his assistants. (1) Dubey (N.R.C. 1931); (2) Holmes and Paneth (1936); (3) Lane and Urry (1935), Urry (1936); (4) Goodman and Evans (1941); (5) Hurley and Goodman (corrected values calculated from their reported analyses); (6) Strutt (N.R.C. 1931); (7) Kano (N.R.C. 1931); (8) Davis (N.R.C. 1931); (9) Lange (N.R.C. 1931). Several of the helium indices have been checked by different observers. In all cases where *A* was greater than 500 million years, the effect of the decay of the parent elements with time was taken into account.

The bulk of the results on granitic rocks, lavas, porphyries, and on minerals were obtained by the writer, most of the results on basic rocks by Urry (1936). The latter results have been corrected by applying corrections of +237 per cent to the radium values and −16 per cent to the helium values previously published (Evans and others, 1939). When this is done the results are in general agreement with age determinations and recalibrations made by the writer.

If there were no gain or loss of helium or of radioactive material, the ratio of $I/A$ should be unity. If helium escaped from the mineral, the ratio would be less than one, if helium were present at the time of crystallization, the ratio would be greater than one.

In view of the prominence given to errors and discrepancies in earlier results, it is interesting to note that the average values of retentivities obtained in different laboratories are not in disagreement (Table 3). The results of earlier investigations are some-

TABLE 3

SUMMARY OF RETENTIVITY DATA FROM DIFFERENT LABORATORIES

| TYPE OF SAMPLE | STRUTT, HOLMES AND EARLIER INVESTIGATORS | | URRY | | GOODMAN | | HURLEY | | KEEVIL | |
|---|---|---|---|---|---|---|---|---|---|---|
| | No. | Av. | No. | Av. | No. | Av. | No. | Av. | No. | Av. |
| Granitic rocks | 1 | ... | 3 | 0.36 | 2 | ... | .. | ... | 34 | 0.25 |
| Basic rocks... | 13 | 0.37 | 47 | 0.47 | 8 | 0.46 | 1 | ... | 18 | 0.44 |
| Porphyries and lavas... | 1 | ... | 3 | 0.37 | 5 | 0.21 | .. | ... | 22 | 0.12 |
| Oxy-salts and halides..... | 5 | 0.38 | 5 | 0.38 | .. | ... | .. | ... | 12 | 0.45 |
| Magnetite.... | .. | ... | .. | ... | .. | ... | 18 | 0.93 | 10 | 0.46 |
| Quartz....... | .. | ... | .. | ... | .. | ... | .. | ... | 14 | 0.25 |
| Other oxides.. | 17 | 0.25 | .. | ... | .. | ... | .. | ... | 6 | 0.32 |
| Feldspar...... | .. | ... | .. | ... | .. | ... | 2 | ... | 25 | 0.20 |
| Femics....... | 2 | ... | .. | ... | .. | ... | 2 | ... | 37 | 0.57 |
| Other silicates | 27 | 0.34 | 2 | ... | .. | ... | .. | ... | 22 | 0.41 |
| TOTALS | 66 | 0.32 | 60 | 0.44 | 15 | 0.35 | 23 | 0.84 | 200 | 03.4 |
| High values discarded. | 2 | | 5 | | 1 | | 10 | | 14 | |

what surprising since they include many radioactive and metamorphic minerals which would tend to yield lower retentivity values. That these results should be discarded because of helium leakage, and more recent results accepted, as suggested by Goodman and Evans (1941), is therefore not justified. There is, however, some reason to doubt the experimental accuracy of the earlier measurements. Similarly, the corrected helium indices determined by Urry do not disagree with recent data and therefore should not be discarded *en masse* as done by Goodman and Evans. However, the comparability of recent measurements and the reliability of the experimental methods have been established (Evans, Goodman, Keevil, Lane, and Urry, 1939), and whether or not the earlier results are excluded because of suspected errors, the conclusions reached in this paper regarding the unreliability of the helium method are unchanged.

## LOSS OF HELIUM

It is evident from Table 2 that more than 90 per cent of the samples of typical igneous rocks and minerals which have been studied show values of $I/A$ which are less than unity. The obvious explanation for this phenomenon is that helium has escaped from its source during geological time, in which case $I/A$ measures the degree of retention of helium, or the *helium retentivity*. There is good reason to believe that the unequal migration of helium from different minerals *is* the cause of the variations in helium index results, in fact this is suggested by most previous work.

It has been shown experimentally (Braaten and Clark, 1935) and theoretically (Keevil, 1940), that helium can diffuse through silicate glasses; and in actual determinations on rocks low results have been obtained when a glassy or cryptocrystalline ground-mass was present. The following results on three lavas from the Lake District, England, of established Ordovician age show beyond doubt that helium has escaped, or radioactive material been added:[2]

| | HELIUM INDEX | EXPECTED AGE |
|---|---|---|
| Basic lava | 5 | 380 |
| Stockdale rhyolite | 15 | 380 |
| Amygdaloidal lava | 26 | 380 |

---

[2] Making the usual assumption that the rates of radioactive disintegration are not changed significantly by geological processes.

The possibility of the introduction of radioactive matter is extremely remote, as indicated by the generally low results obtained with other porphyries and lavas (Table 4) in contrast to the higher results found for granitic and basic rocks. Thus far, attempts to force helium to diffuse through crystals of common rock minerals have been unsuccessful, and theoretical calculations have shown that for ideal structures with no concentration gradient, the migration of helium would be negligible (1940). It was shown, however, that self-diffusion of helium might occur with relatively small changes in interatomic distances which would provide openings comparable in size with those present in silicate glasses. The results reported in this paper suggest that such imperfections in structure are more extensive than was formerly believed.

It has been found that helium index values of metamorphic rocks are much lower than those of unaltered rocks of comparable age, indicating loss of helium during metamorphism. Low results have also been obtained for rocks altered by deuteric solutions, by mineralization, and by weathering agencies, perhaps due to loss of helium during alteration, or to later migration from the altered minerals and interrupted structures of secondary minerals.

Recent results have also indicated a greater localization of radioactivity than was previously believed to exist; this would result in concentration gradients of helium, as well as causing local ruptures of crystal structure, both of which factors would favour migration. Although preliminary experiments on a weakly radioactive Californian granite of late Jurassic age suggested a fairly uniform distribution of radioactivity, more detailed investigations showed that most of the radioactive elements are concentrated in the zircon, apatite, and sphene which comprised only one-quarter of one per cent of the rock (Larsen and Keevil, 1941). The lowest helium index values were obtained from the accessory minerals; and since the concentrations of helium were relatively high in these three minerals, it is probable that the discrepancies are due to the diffusion of helium from its radioactive source. In Table 4 (fourth column), the relative radioactivities provide a measure of the relative quantities of helium produced within the various minerals.

Such variations in the helium indices of the constituent minerals in rocks appear to be general. Frequently, the lowest values were

TABLE 4

RADIOACTIVE ACCESSORIES IN A CALIFORNIAN TONALITE

| MINERAL | WEIGHT PER CENT | RADIOACTIVITY PER CENT | RADIOACTIVITY RATE* | HELIUM INDEX |
|---|---|---|---|---|
| Zircon......... | 0.02 | 12.8 | 1030 | 23 |
| Sphene........ | 0.04 | 17.1 | 680 | 30 |
| Apatite........ | 0.20 | 17.9 | 140 | 43 |
| Hornblende.... | 13 | 16.2 | 2.0 | 200 |
| Magnetite...... | 1 | 0.9 | 1.6 | .. |
| Biotite......... | 18 | 11.7 | 1.0 | 91 |
| Plagioclase..... | 49 | 18.0 | 0.6 | 41 |
| Quartz......... | 20 | 5.4 | 0.4 | 74 |

*Relative to biotite.

found in minerals which have contained the least radiogenic helium, indicating some relationship between leakage and the type of mineral (Table 5).

TABLE 5

UNEQUAL MIGRATION OF HELIUM THROUGH DIFFERENT MINERAL CONSTITUENTS OF ROCKS

| ROCK | LOCALITY | MINERAL | PRODUCTION OF HELIUM RELATIVE TO FELDSPAR | HELIUM INDEX | EXPECTED AGE |
|---|---|---|---|---|---|
| Granite | Quincy, Mass. | Feldspar | 1 | 49 | |
| | Quincy, Mass. | Quartz | 1 | 86 | 240 |
| | Quincy, Mass. | Pyroxenes | 4 | 86 | |
| Granite | Rockport, Mass. | Feldspar | 1 | 64 | |
| | Rockport, Mass. | Quartz | 2 | 102 | 275 |
| | Rockport, Mass. | Biotite and Hornblende | 14 | 183 | |
| Diabase | Yellowknife, N.W.T. | Feldspar | 1 | 101 | |
| | | Pyroxene | 1 | 1310 | 600 |
| | | Magnetite | 1 | 7350 | |
| Granite | Yellowknife, N.W.T. | Feldspar | 1 | 158 | |
| | | Quartz | 1.5 | 147 | 900 |
| | | Biotite and Hornblende | 8 | 594 | |

Whether the variations in helium index are due to differences in crystal structure or to crystal imperfection and alteration, or to other causes, cannot be decided at present. However, variations which have been found between results for different samples of the same mineral from the same locality indicate that the first cause is improbable.

These few illustrations suggest that helium produced within minerals may migrate from its source, and that loss takes place to different extents in different types of rocks and minerals and even in different specimens of the same material.

In a few cases, loss of helium from certain minerals has been found after standing, for example, from a granite specimen and its constituent quartz and feldspar after one year in the laboratory:

| | GRANITE | QUARTZ | FELDSPAR |
|---|---|---|---|
| Helium Index at time of collection... | 95 | 157 | 74 |
| Helium Index after one year........ | 72 | 94 | 47 |
| Per cent loss (exp.)............... | 24 ± 15 | 40 ± 20 | 37 ± 15 |
| Per cent loss (calc.)............... | 22 | — | — |

No loss from femic minerals was found.

Similar tests on various rocks have given conflicting data, but it can be concluded that, on the whole, the loss of helium during preliminary laboratory treatment is negligible, and that the low retentivities are largely due to loss of helium under normal geological conditions.

## EXCESS HELIUM IN MINERALS

Against the assumed time scale, helium index values are found to be predominantly low. However, in a few cases—approximately 1 in 20—evidence of excess helium has been observed. The occasional presence of greater quantities of helium in tightly packed atomic structures suggests a magmatic source, or a source within the mineral. Since helium does not appear to be concentrated in minerals of open structure, it probably escapes along the easier path of the interstices. In view of the significance attached to magnetite (Hurley and Goodman, 1941), the ages found for magnetites separated from Keweenawan diabase specimens afford striking examples of excess helium.

| | |
|---|---|
| First sample | 2,640 |
| Second sample | 16,500 |
| Expected value | 600 |

### INTRODUCTION OF RADIOACTIVE MATTER AFTER CONSOLIDATION

Since a low helium index may result from contamination by radioactive matter as well as from loss of helium, this possibility must be given consideration. It is believed that contamination during laboratory procedures is negligible, but the addition of radioactive material by geological processes may occur. The writer has found that mineralized areas around some ore-bodies possess higher radioactivities than the normal country-rock, and evidence has also been found of excess radioactivity in certain migmatites. In such isolated cases, one would expect the helium index to be lowered, but it is extremely unlikely that any appreciable number of the low "retentivities" are due to radioactive contamination. A consideration of the distribution of helium in rocks, the uniformity of helium index results from specimens distributed across some intrusives, the frequent association of most of the radioactivity in the early accessories, and the low activity of some minerals altered by deuteric processes, all suggest that the low results are not due to secondary enrichment by relatively radioactive solutions.

### THE UNRELIABILITY OF AVERAGE RETENTIVITIES IN CALCULATING HELIUM AGES

Now that it is established that helium indices are generally low, the value to geochronology of correcting these results by using average retentivities should be considered. It may be assumed that large excesses of extraneous helium would be detectable and that other cases of contamination by helium would be too infrequent to cause much uncertainty.

Fig. 1 shows frequency distribution curves for porphyries and lavas, granitic, and basic rocks. The most probable values of helium retentivities are:

| | | |
|---|---|---|
| Porphyries and lavas | 0.045 | (0.030 to 0.127) |
| Granitic rocks | 0.24 | (0.16 to 0.37) |
| Crystalline basic rocks | 0.45 | (0.125 to 0.585) |

the mean values being 0.094, 0.28, and 0.46 respectively. These values and their limits of probable error determined from the curves show that helium index values corrected for leakage on the basis of average helium retentivities would be of only limited use in geological correlation. Application of these results to rocks dated by the scale in Table 1 shows that, at best, there is only an even chance of determining the age with an error of less than one geological period. For example, the limits of probable error of a Triassic diabase would extend from the Permian to late Jurassic, for granites the limits would be somewhat larger, and for porphyries and glassy lavas, the results would be meaningless.

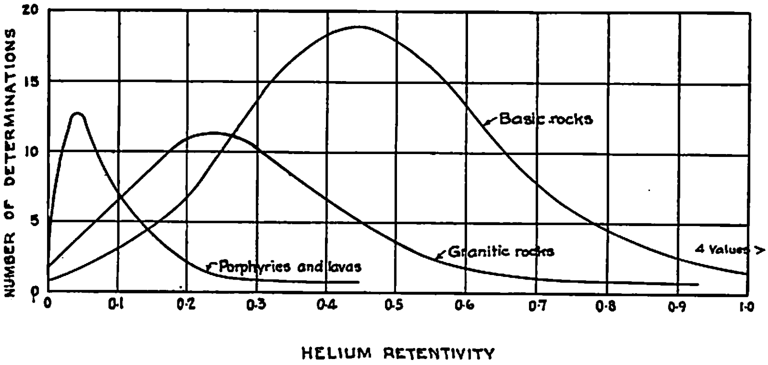


FIG. 1.—Frequency distribution curves of helium retentivity in rocks.

## FAILURE TO OBTAIN EXPECTED SEQUENCE

Due to differences in geological history in different regions, it is not quite fair to use average values of retentivity. It might be expected that rocks from one particular area would show smaller variations than those indicated in the foregoing paragraphs. To show the limitations of the applicability of helium index determinations in problems of local correlation, several series of data are summarized in Table 6.

These results show roughly that local applications to crystalline igneous rocks are a little more reliable than inter-regional applications, but the chance of finding the correct sequence remains only

## TABLE 6

### RESULTS IN LIMITED AREAS

| LOCALITY | GEOLOGIC SEQUENCE | HELIUM INDEX |
|---|---|---|
| *East Coastal Granites* | | |
| Fitchburg, Mass. | 1 | 43 |
| Chelmsford, Mass. | 1 | 68 |
| Quincy, Mass. | 2 | 62 |
| Cape Ann, Mass. | 2 | 100 |
| Hampstead, N.B. | 3 | 104 |
| St. George, N.B. | 3 | 94 |
| Nipisiguit, N.B. | 3 | 41 |
| Franklin, Me. | 4 | 55 |
| *Rouyn Acidic Intrusives* | | |
| Taschereau, Que. | 1 | 70 |
| Flavrian L., Que. | 1 | 226 |
| Taschereau, Que. | 2 | 234 |
| Flavrian L., Que. | 2 | 208 |
| Lake La Motte, Que. | 2 | 170 |
| Varsan Tp., Que. | 3 | 945 |
| *Tanganyika Intrusives* | | |
| Granite | 1 | 21 |
| Granite | 1 | 185 |
| Aplogneiss | 2 | 21 |
| Granodiorite | 2 | 240 |
| *Red Lake, Ontario* | | |
| Post-ore dike | 1 | 131 |
| Pre-ore dike | 2 | 136 |
| Quartz porphyry | 1 | 49 |
| Altered diorite | 2 | 129 |
| *Hornblende Concentrates* | | |
| Post-ore dike | 1 | 243 |
| Pre-ore dike | 2 | 243<br>530 |
| Granodiorite | 3 | 315<br>498 |
| Pyroxenite | 4 | 988 |
| Hornblende diorite | 5 | 78<br>1060 |
| Diorite | 6 | 206 |
| *Blue Mountain, Ontario* | | |
| Syenodiorite | 1 | 160 |
| Litchfieldite | 2 | 800 |
| *Kingston Area, Ontario* | | |
| Red granite | 1 | 233 |
| Pink granite | 1 | 140 |
| *B.C. Granitic Rocks* | | |
| Castle Peak stock | 1 | 56 |
| Shuswap gneiss | 2 | 37 |
| Shuswap granite | 2 | 84 |
| *Californian Intrusives* | | |
| Riverside granodiorite | 1 | 66 |
| Bonsall tonalite | 2 | 27 |
| Lakeview tonalite | 3 | 77 |
| *Buchans, Newfoundland* | | |
| Post-ore diabase | 1 | 59 |
| Ore (barite) | 2 | 80 |
| Pre-ore diabase | 3 | 69 |
| Pink granite | 4 | 93 |
| Grey granite | 5 | 141 |
| Amphibolite | 6 | 332 |
| Porphyries | 7 | 21 |
| Lavas | 7 | 8-59 |
| *Eustis Mine, Que.* | | |
| Post-ore lamprophyre | 1 | 52 |
| Pre-ore lamprophyre | 2 | 77 |
| *Franklin, N.J.* | | |
| Young trap | 1 | 150 |
| Various minerals | 2 | 75-15400 |
| Pochuk gneiss | 3 | 131 |

TABLE 6—(*Continued*)

| LOCALITY | GEOLOGIC SEQUENCE | HELIUM INDEX |
|---|---|---|
| *Yellowstone Park* | | |
| Porphyritic basalt | 1 | 5 |
| Tower Falls basalt | 1 | 6 |
| Crescent Hill basalt | 1 | 9 |
| Overhanging Cliff basalt | 1 | 11 |
| Geode Creek basalt | 2 | 36 |
| Long Lake diabase | 3 | 85 |
| Bear-tooth trap | 3 | 226 |
| Bear-tooth trap | 3 | 1050 |
| Stillwater norite | 4 | 1920 |

| LOCALITY | GEOLOGIC SEQUENCE | HELIUM INDEX |
|---|---|---|
| *Attleboro Lavas* | | |
| Basalt | 1 | 22 |
| Rhyolite | 1 | 47 |
| *Yellowknife, N.W.T.* | | |
| Diabase | 1 | 1160 |
| Granite | 2 | 125 |
| Granite | 2 | 371 |

about 60 per cent, too small to be of general geological use. In some cases the geological probable errors may be high enough to warrant helium index investigations, but the caution that must be exercised in interpreting the results is indicated by the following example of observed discrepancies:

GARNETS FROM FORT WRANGEL, ALASKA

| | |
|---|---|
| First crystal | 56 ± 15 |
| Second crystal | 130 ± 40 |
| Third crystal | 350 ± 40 |

These variations may be due to inclusions and unequal imperfection of the garnet structures in the three crystals; nevertheless, such differences found for single crystals of identical appearance indicate the futility of using helium indices directly as a tool in geological correlation.

## A RAY OF HOPE FOR THE FUTURE

It is apparent that no type of rock or mineral can be said to be generally suitable for reliable helium age determinations. The nature of the fluctuations found in abundant results on a variety of representative samples suggests that several variables affect the retentivity of helium and that these are operative on all types of rocks and minerals. The data plotted in Fig. 2 show that one or more of these variables is related to time. The results are scattered but there does seem to be less retention in older than in younger rocks. That geological processes would have such an effect is to be expected, and it is reasonable to assume that the variation is related to the degree of alteration, visible and invisible.

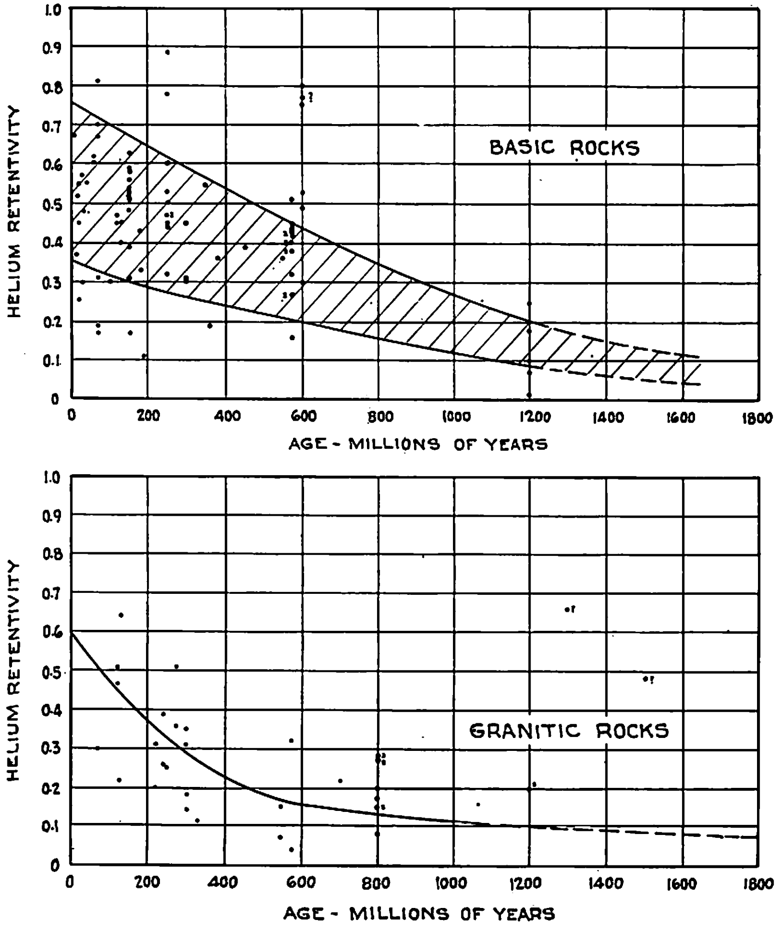


FIG. 2.—Plot of helium retentivity against age suggesting loss of helium due to geological processes.

Study of the variations in some helium index results and observations of the character of the specimens have disclosed a relationship between the helium index and the degree of alteration, extent of metamorphism, amount of weathering, texture, and type of mineral. Other factors may also enter. It is possible that experimental values of the helium index may be corrected for the effects of these variables, once these relationships are known. Preliminary results indicate that the probable error may be reduced considerably by correcting for the effects of alteration on helium retentivity, but no consistent procedure has been developed. The magnitude of the task is indicated by the following examples:

| | | |
|---|---|---|
| Keweenawan diabase... | (slightly altered) 226; | (highly altered) 85 |
| Algoman granite....... | (medium alteration) 502; | (extensive alteration) 315 |
| Algoman diorite....... | (slightly altered) 1060; | (highly altered) 78 |

Of course the errors may be reduced by selection of the least altered samples, and by the use of comparable minerals; however, whether a *general* relationship exists between helium leakage and degree of alteration is still unknown, and it is uncertain whether a reliable method of finding the degree of alteration can be developed. Some uncertainty also exists in the degree of reproducibility of results on apparently unaltered crystals of the same mineral.

The writer is at present commencing work on the lead age method but is continuing to devote some time to an investigation of the effects of various kinds of alteration on helium retentivity. At the present stage no new problems are being undertaken in helium age work unless some promise of success in correlation, or of gaining more fundamental knowledge, is foreseen.

## SUMMARY

Two hundred new determinations of geological age on rocks and minerals by the helium method, together with 165 previous determinations by others, are reduced to a common basis and compared with the most reliable available time scale. The ratio of the measured age to the expected age ($I/A$) ranges from 0.01 to 25, giving a variation of 1 to 2500. No type of rock or mineral, including magnetite, gives consistent results. Such discrepancies cannot be explained by experimental errors, which are about 10 per cent.

Since the ratio $I/A$ is generally less than unity, indicating a variable loss in helium, this ratio is termed the helium retentivity. Variation in helium retentivity may be due to geological history, (metamorphism, deuteric processes, mineralization, weathering), interruptions of crystal structure, or localization of helium in accessory minerals; introduced radioactive mätter would also reduce the term *I*. Rarely *I*/*A* is greater than unity; this may be due to helium or short-lived radioactive elements trapped during crystallization. Ages (*I*) corrected with reference to the most probable retentivity values given by frequency curves, fail, more often than not, to place a given rock or mineral in the expected geological system. The helium method offers little promise of usefulness unless more effective methods of interpretation are devised.

## REFERENCES

BRAATEN, E. O. and CLARK, G. F. (1935): The diffusion of helium through fused silica—*Jour. Am. Chem. Soc.*, vol. 57, pp. 2714-2717.

EVANS, R. D., GOODMAN, C., KEEVIL, N. B., LANE, A. C., and URRY, W. D. (1939): Intercalibration and comparison in two laboratories of measurements incident to the determination of the geological ages of rocks—*Phys. Rev.*, vol. 55, pp. 931-946.

GOODMAN, C. and EVANS, R. D. (1941): Age measurements by radioactivity—*Bull. Geol. Soc. Am.*, vol. 52, pp. 491-544.

HOLMES, A. and PANETH, F. A. (1936): Helium-ratios of rocks and minerals from the diamond pipes of South Africa—*Proc. Roy. Soc. London*, vol. 154 A, pp. 385-413.

HURLEY, P. M. and GOODMAN, C. (1941): Helium retention in common rock minerals—*Bull. Geol. Soc. Am.*, vol. 52, pp. 545-560.

KEEVIL, N. B. (1938a): The application of the helium method to granites—*Trans. Roy. Soc. Canada*, vol. 32, sec. 4, pp. 123-150.

———— (1938b): The distribution of helium and radioactivity in rocks, I. Mineral separates from the Quincy granite—*Am. Jour. Sci.*, vol. 36, pp. 406-416.

———— (1940): Interatomic forces and helium in rocks—*Proc. Am. Acad. Arts Sci.*, vol. 73, no. 11, pp. 311-359.

———— (1941a): Helium retentivities of minerals—*Am. Mineral.*, vol. 26, pp. 403-404.

———— (1941b): Terminology in age work—*Am. Jour. Sci.*, vol. 239, pp. 608-611.

LANE, A. C. and URRY, W. D. (1935): Ages by the helium method: I. Keweenawan—*Bull. Geol. Soc. Am.*, vol. 46, pp. 1101-1120.

LARSEN, E. S. and KEEVIL, N. B. (1941): Radioactivity and petrology of some California intrusives—*Am. Jour. Sci.* (submitted for publication).

NATIONAL RESEARCH COUNCIL (1931): *Age of the earth*, Bull. 80, private printing.

URRY, W. D. (1936): Ages by the helium method: II. post-Keweenawan—*Bull. Geol. Soc. Am.*, vol. 47, pp. 1217-1234.

# REMARKABLE MOULDS OF HOPPER-SHAPED HALITE CRYSTALS FROM MANITOBA

By E. Leith
*University of Manitoba*

In the geological collections of the University of Manitoba there are two limestone boulders with beautifully preserved, large, and nearly complete moulds of hopper-shaped halite crystals or, as they are commonly called, salt hoppers. I am indebted to Dr. R. C. McMurchy[1] for the information that one of the boulders (Fig. 1) was collected in the area between Lake Winnipeg and

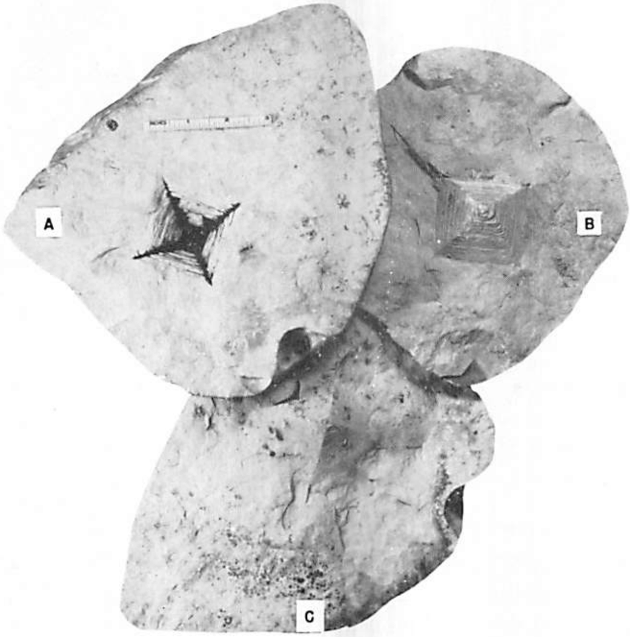


Fig. 1.—Limestone boulder (specimen number 105, University of Manitoba) with mould of halite crystal consisting of three slabs A, B, and C. The "pyramids" on slabs B and C fit into the area covered by the black "X" of slab A and on its upper and lower sides respectively.

---

[1] Powell Rouyn Gold Mines, Noranda, Quebec. Personal communication.

Lake Manitoba by a farmer and was given to the late Professor S. R. Kirk of the University of Manitoba. Although information is not available concerning the second boulder described here, it very likely was also collected in the region between Lakes Winnipeg and Manitoba.

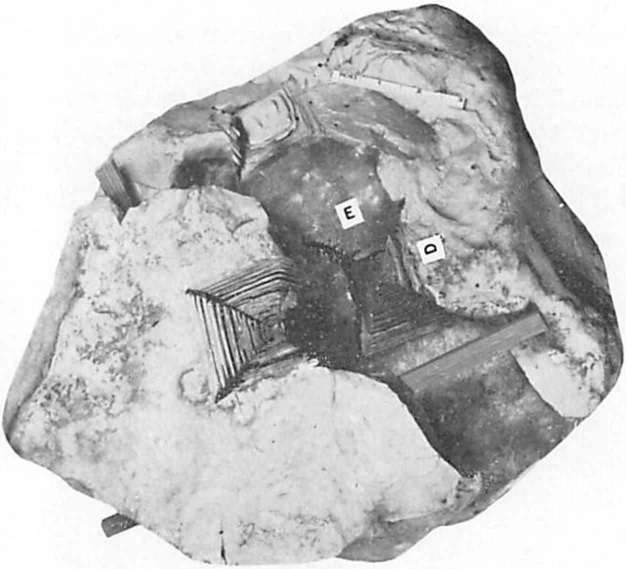


FIG. 2.—Limestone boulder (specimen number 106, University of Manitoba) with moulds of halite crystals. The boulder consists of two parts with the one part being slightly elevated above and separated laterally from the other by two narrow strips of wood to show the nearly complete mould of the halite crystal in the centre of the block.

The limestone making up the boulders is yellowish-white in colour on a freshly broken surface, grayish-white on the weathered surface and is almost lithographic stone in texture. Both specimens appear to be field boulders and probably were in the glacial drift of the area between the lakes. The boulders appear to have been derived from limestones in the Stonewall Series of Silurian age.

Each crystal of halite was cubical with a very deep hopper-shaped depression developed on each face of the cube. The apices of the hoppers appear to have almost met at the centre of the cube. After complete burial in the lime mud, with the hopper-shaped depressions also completely filled in with the mud, the entire mass was lithified. By subsequent solution of the halite only the cavity representing the true crystal form and the moulds of the hopper-shaped depressions were left, and these features are shown in the accompanying photographs. The moulds of the hopper-shaped depressions now appear as pyramid-like structures and the deep black colour in the illustrations appearing as an X, particularly well shown by Fig. 5, indicates the cavity left by the solution of the halite. The length of the cube edge in the largest specimen is 2.8 inches and in the smaller specimen 2.3 inches.

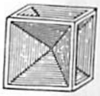


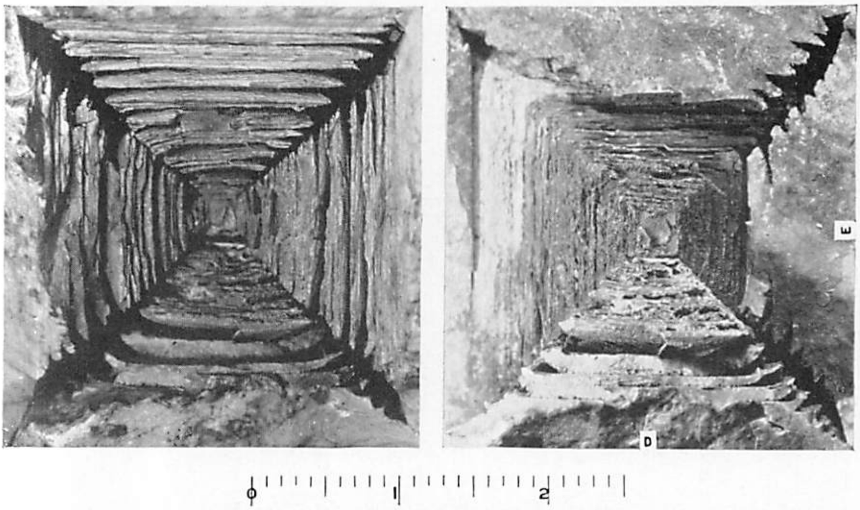
FIG. 3 (centre).—Hopper-shaped halite crystal after Moses and Parsons. For purposes of description of figures 6 and 7, the top, bottom, front, and sides of the cube have been arbitrarily selected.

FIG. 4 (left).—Pyramid-like mould of hopper-shaped depression of one side of a halite crystal. See B, fig. 1.

FIG. 5 (right).—Moulds of five of the hopper-shaped depressions of a halite crystal and cavity left by solution of halite. This view is slab A placed over slab C (see fig. 1).

The origin of hopper-shaped halite crystals or salt hoppers has been described by Vanuxem (1842, p. 102) and Kindle (1918, p. 476), and their discussions need not be repeated here.

Salt hopper moulds have been collected by the writer in the Camillus shale (Upper Silurian) of New York. The specimens are usually moulds of only one face of the hopper-shaped depressions. A few of the moulds collected show that several crystals were developed in a small space and these mutually interfered with one another in their growth so that perfect cubes were not developed.



FIGS. 6 and 7.—Mould of a halite cube and cavity left by solution of halite. FIG. 6 (left).—Moulds of the hopper-shaped depressions of the top, bottom, and sides of the cube. The mould of the front is missing from the specimen. View taken of boulder illustrated as fig. 2 without separation of the two parts of the boulder. FIG. 7 (right).—View to show pyramid-like mould of the hopper-shaped depression of the back of the cube. The moulds of the bottom and parts of the side and top of the cube are also included in this view. See fig. 2 for corresponding positions of letters D and E.

Vanuxem (1842, p. 102) has described and illustrated the mould of a complete single hopper-shaped depression and one-half of a cube from the Upper Silurian of New York. The salt hoppers from New York are 1-3 inches or more in diameter. Several small pseudomorphs of salt crystals with hopper-shaped depressions found in Cambrian limestone at Jasper Park, British Columbia, have been described and illustrated by Kindle (1918, p. 476).

Daly (1912, p. 82) has described hopper-shaped salt crystals from the Kintla (Beltian) formation of British Columbia. The specimens just listed, however, do not attain the remarkable preservation and complete form exhibited by the Manitoba salt hopper moulds.

## REFERENCES

DALY, R. A. (1912): Geology of the North American cordillera at the forty-ninth parallel—*Geol. Surv. Canada*, Mem. 38, pt. 1.

KINDLE, E. M. (1918): Separation of salt from saline water and mud—*Bull. Geol. Soc. Am.*, vol. 29, pp. 471-488.

MOSES, A. J. and PARSONS, C. L. (1920): *Elements of mineralogy, crystallography and blowpipe analysis*, ed. 5—New York.

VANUXEM, L. (1842): *Geology of New York*, Part 3, *Geology of the Third District*—Albany, N.Y.

# ANHYDRITE AND GYPSUM AT CALUMET MINES CALUMET ISLAND, QUEBEC[1]

By F. Fitz Osborne
*McGill University*

## Introduction

The property of Calumet Mines, Limited, is on the west side of Calumet Island, which is in the Ottawa River about sixty miles above Ottawa. Although the occurrences of zinc-lead ore have long been known, the recent campaign, in which 100,000 feet of diamond drilling was done, has given valuable additional data on the complex geology of the region, which is a part of the Grenville sub-province of the Canadian shield, although some of the features encountered in drilling are distinctly unusual in that sub-province. One unusual feature is the occurrence of anhydrite and gypsum, which were found in deep drill-holes principally in Grenville crystalline limestones. It is not necessary to discuss the geology of Calumet Island in detail for the purposes of this paper.

The Grenville limestones crop out along the channel of the Ottawa River which forms the boundary between Ontario and Quebec near Calumet Mines. On the east, bluffs of meta-sedimentary silicate rocks of the Grenville series rise steeply above the river. The limestones dip 30° E. and pass structurally beneath, but do not necessarily stratigraphically underlie, the silicate rocks. A drill-hole 4,500 feet east of the outcrop proves that the dip is uniform and that the limestones continue beneath the silicates at least to that point. Another drill-hole 3,000 feet east of the outcrop passed through 550 feet of Grenville limestone, and it is the cores from this hole that have the most anhydrite.

The drilling has served to outline a principal ore-bearing horizon that is parallel to the general structure as defined by the plane of contact between limestone and silicate rocks, and about 700 feet vertically above the hanging-wall of the limestone. This accounts for the fact that only two holes reached the limestone, and only one passed through a considerable thickness of it. No ore-shoots

---

[1] Published with the permission of the Director, Quebec Bureau of Mines.

are known below the principal zone mentioned; but the drill-hole 3,000 feet east of the outcrop passed through a narrow zone of disseminated sphalerite in carbonate 130 feet below the upper limit of the limestone, and similar disseminated sphalerite is exposed on the river's edge at about the same structural position. Disseminated pyrite with a trace of sphalerite was found in limestone near the bottom of the deeper hole. Although these occurrences are not economically interesting, they may be significant in that they occur in the same section as the anhydrite.

## ANHYDRITE

The anhydrite first attracted attention in the cores on account of its tendency to dissolve or abrade more than the silicate or carbonate minerals. The cores with anhydrite show depressions on the surface although the depressions are shallower than those formed in gypsum. The anhydrite is in several forms: a pale-violet to colourless variety mixed with carbonate of the same granularity and forming perhaps 60 per cent of the aggregate; elsewhere the anhydrite is deep mauve to brownish and coarsely crystalline. The full size of the crystals is indeterminate, because the specimens are in cores obtained with an *E*-size bit, but they probably are as much as two inches in diameter. A third mode of occurrence is with coarse-grained salmon calcite containing diopside, apatite, and phlogopite. This type of calcite with the associated minerals is exposed on the river bank and may be observed to fill tension cracks in the silicate rocks; but if anhydrite was present it has been dissolved. The fact that exposures of these veins are cavernous suggests that it was originally present.

All the thin sections examined show that anhydrite has replaced carbonate, apparently calcite. Furthermore, the relic carbonates and the associated silicates, largely diopside, show a texture that is characteristic of the crystalline limestones. No instance was observed in which silicates were replaced by anhydrite. Although in a few places anhydrite is enclosed in diopside, it is clear that the diopside contained poikiloblastic carbonate. The anhydrite is clear and shows the characteristic cleavages and twinning. In many places the twinning is polysynthetic, and it is especially common in sections showing much hydration of the anhydrite to yield gypsum.

## Gypsum

Gypsum is found as an alteration product of anhydrite. Thin sections show all stages of the process, which appears to start near the margins of the anhydrite and extend inward. Aggregates of plumose gypsum fringe many of the grains of anhydrite, and the orientation of the crystals appears to be independent of that of the anhydrite, although in some sections the gypsum has replaced the anhydrite along twin planes. The lack of orientation may not be significant, since Fairbairn (1935) has suggested that some re-orientation of gypsum may take place during the grinding of a section.

In thin sections of gypsum with anhydrite there is no evidence that gypsum replaced calcite or silicates. But in amphibolites above the limestone, gypsum has replaced relic calcite. In these occurrences, however, there is no trace of anhydrite.

Gypsum is more widely distributed than the anhydrite because it is found as veinlets in the silicate rocks, separating the ore-bearing horizon from the limestones, and even in small amounts above the ore-zone. In the cores, the gypsum is in veinlets $\frac{1}{32}$ to $\frac{1}{8}$ inch wide which are noticeable because of the deep etching. A few of the veinlets are parallel to the schistosity, but most of them are inclined. No anhydrite is present in the veinlets. The gypsum replacing carbonate enclosed in the silicate rock is found in only a few places. Narrow veins, with the plumose gypsum extending from wall to wall, represent the characteristic mode of occurrence.

## Age of the Sulphates

It is obvious from the textures of the limestones that the anhydrite post-dates the major deformation, and it is equally clear that the gypsum has replaced anhydrite. Veinlets of gypsum were observed to cut grains of serpentine in de-dolomitized limestone and also to cut anhedra of sphalerite and crystals of pyrite, but the age of the anhydrite could not be established with certainty.

## Origin of Gypsum

From the general relationships it is clear that the gypsum is derived from anhydrite. The reaction is:

$$CaSO_4 + 2H_2O = CaSO_4.2H_2O$$

A formula weight of anhydrite with a volume of 46 c.c. will give a formula weight of gypsum with a volume of 74 c.c. The increase in volume with the formation of gypsum, and the lack of evidence of volume increase by deformation in the anhydrite-bearing limestone, suggest that gypsum, the phase stable in the solution pervading the rock, was removed and deposited in the minute cracks at higher levels. The increase in volume, and consequently the increase in pressure on the solid, would naturally increase the solubility of the sulphate. The sections examined suggest that the gypsum was the only constituent to be deposited by the solutions causing hydration, and that alteration of the walls was negligible. In only a few places was calcite replaced and for these occurrences it is only the absence of relic anhydrite that suggests that gypsum replaced calcite rather than anhydrite. The considerable amounts of gypsum formed from anhydrite, found in the 600-foot long section of the limestones, are quantitatively adequate to account for the gypsum found in the 600 feet above the limestone.

## ORIGIN OF ANHYDRITE

The anhydrite has obviously replaced limestones subsequent to their deformation, and this rules out the possibility that the anhydrite was a constituent of the limestones in the position they now have, but the possibility that the Grenville originally had sulphate either as anhydrite or gypsum is attractive because of the well-known occurrences of these minerals in sedimentary series. It is possible that such sulphate could be redistributed by thermal waters. This interpretation has been favoured by Brown (1932, 1936) to account for the anhydrite found near the zinc-lead orebodies at Balmat and Edwards, New York. Dr. Brown has discussed the problem with the writer, and has supplied him with specimens. Inasmuch as Brown's views have been modified as the result of development at Balmat, the presentation here follows the oral discussion by Brown, supplemented by notes received from him in March, 1940.

Brown believes that the Grenville limestones near Balmat originally contained beds of halite and sulphates, and that these constituents were re-arranged. Although anhydrite and halite are found in dykes of gray pegmatite, Brown believes that the layers of the easily-deformed salts determined the position taken by the pegmatites, and that the halite and sulphates show no distinct relationship in space to ore-bodies. Brown states, in a note: "Gypsum, however, is post-sphalerite, chiefly if not entirely. Petrographically, anhydrite seems to be pre-sphalerite." One specimen from Balmat suggests to the writer that Brown's uncertainty concerning the relative ages of sphalerite and anhydrite is well founded, and that his early statement that anhydrite has the same post-sulphide age as barite should not be too summarily rejected.

The alternative to this hypothesis, that the sulphates were an original constituent of the Grenville, is that the sulphates came from a magmatic source. This source of sulphates has been discussed by Butler (1919) who described deposits in a number of localities. He points out that anhydrite and celestite are not rare in "intermediate-temperature veins." Both the Calumet and Balmat deposits are high-temperature types. Two Canadian examples of the occurrence of anhydrite with high-temperature mineral deposits have been described. James (1929) has discussed the distribution of anhydrite along the mineralized shear-zone at the Britannia Mine and has shown that the anhydrite has approximately the same vertical extent as the copper mineralization although the anhydrite is apparently much younger than the ore minerals. Barite, on the other hand, is restricted to the vicinity of a sphalerite-galena occurrence at high levels. Langford and Hancox (1936) have discussed the occurrence of anhydrite in the Porcupine district and they were inclined to consider the formation of anhydrite and gypsum a late stage of the mineralization. At both the Britannia and the McIntyre (Porcupine) Mines, probabilities of gypsum or anhydrite as a constituent of the country rock are negligible, and the appeal to magmatic solutions as a source of sulphate is logical.

In the field season of 1940, the writer examined the surface and drill cores of the Miller claims in the centre of Gaspé. Chalcopyrite is the copper-bearing mineral, and it is associated with pyrrhotite and pyrite. The mineral occurrences are in Devonian sedimentary rocks, which have only a low grade of regional attraction. Near the mineralized area the alteration is intense and is of the high-temperature type. Some minerals typical of contact metamorphism are found, and the mineralization as a whole might be considered pyrometasomatic. The low grade of regional alteration in Gaspé contrasts with the high-grade alteration at both Calumet and Balmat, and the difference probably accounts for the pronounced differences in the texture of gangue and ore at the two types of localities. Veins containing pale-mauve anhydrite occur 1000 feet below the surface. The veins are somewhat crustified and contain quartz with molybdenite and chalcopyrite. The textures suggest that the anhydrite is not far removed in age from the chalcopyrite and molybdenite.

The occurrence of gypsum and anhydrite associated with the intrusives at Mount Royal is of interest in this connection. An alkaline gabbro from chainage 194+90 of the tunnel at Mount Royal was described by Bancroft and Howard (1923) as containing wöhlerite. Closer optical examination and chemical tests show that the mineral is anhydrite. A medium-grained pink pegmatite from near the west portal of the tunnel consists of feldspar and selenite. It would require considerable temerity to suggest that the sulphates are pyrogenetic in these rocks, but the textural relationships of the anhydrite in the gabbro are such that Bancroft and Howard were able to consider it a pyrogenetic mineral, and, if the selenite were quartz, the texture of the pegmatite would be quite normal. Analyses of Monteregian rocks in which sulphate is determined show a greater than average content of this constituent.

The above-mentioned occurrences are sufficient to show that anhydrite can occur near high-temperature mineral deposits or igneous rocks where the sulphate is probably derived from an igneous source. The writer considers it probable that the sulphate of the Calumet deposits came from a magmatic source and that anhydrite is possibly a peripheral alteration related to the zinc-lead mineralization. The probability of some genetic relationship between the anhydrite formed in limestone and the ore-forming solutions is increased by the fact that the two localities that have yielded anhydrite in the Grenville sub-province are near zinc-lead deposits. An argument that might be advanced against this view is that only near ore deposits have the limestones been adequately explored to determine the presence of anhydrite. The Grenville limestones have yielded a sufficient variety of economic products to have been explored fairly closely in places; nevertheless, neither anhydrite nor gypsum has been recorded, in spite of the diagnostic physical characteristics of these minerals.

After the sulphates in the core were identified, it was felt advisable to examine the exposures of the band of limestone, to see if there were any indication of the presence of sulphates in the weathering pattern. In most localities where Grenville limestone is exposed in a stream channel, there is little difference in the rate of removal of limestone and dolomite, but both rocks are more easily removed than the silicate-bearing layers. Pitting is characteristic along joint directions, and, in some places, the joints may be markedly etched. The weathering of the Grenville along a section west of the Calumet Mines property is normal in most respects, but, in addition to the usual pitting, there is a series of crevasse-like pits that appear to be independent of the major joints and the foliation. It is believed that the unusual openings are the result of etching of sulphate-bearing layers. It is noteworthy that the region of these pits is opposite to the mineralized zone and that they are not found elsewhere. On account of the etching, it could not be determined whether sulphates were actually present. A number of veins of salmon-pink calcite with phlogopite and diopside occur in the exposures along the river. Many of them show cavernous weathering which may have been the result of removal of sulphate. Calcite in the veins is pitted but not removed to any great extent.

## CONCLUSIONS

At both Calumet and Balmat, the anhydrite is not closely related in space to the zinc-lead ore-bodies. At Balmat, barite is a gangue mineral, and at Calumet, Brown has shown $BaSO_4$ in the analyses of some samples taken in 1935. The writer has identified barite in a thin section of the ore. James's observations at Britannia, that the barite is found with the sphalerite and galena and that anhydrite is co-extensive with chalcopyrite and pyrrhotite, are significant. It may be that the conditions for deposition of barite are similar to those for zinc and lead sulphides but unlike those for anhydrite. Anhydrite may appear, therefore, as a peripheral phase of the alteration near zinc-lead deposits.

The evidence afforded by the geographical distribution of the anhydrite in the Grenville, coupled with the evidence that anhydrite occurs near mineral deposits in non-sulphate-bearing country-rock, suggests that it came from a magmatic source.

## REFERENCES

BANCROFT, J. A. and HOWARD, W. V. (1923): The essexites of Mount Royal, Montreal, P.Q.—*Trans. Roy. Soc. Can.*, vol. 17, sec. 4, pp. 13-43.

BROWN, J. S. (1932): Natural gas, salt, and gypsum in Precambrian rocks at Edwards, New York—*Bull. Am. Ass. Petrol. Geol.*, vol. 16, pp. 727-735.

———— (1936): Structure and primary mineralization of the zinc mine at Balmat, New York—*Econ. Geol.*, vol. 31, pp. 233-258.

BUTLER, B. S. (1919): Primary hypogene sulphate minerals in ore deposits—*Econ. Geol.*, vol. 14, pp. 581-609.

FAIRBAIRN, H. W. (1935): A petrofabric analysis of gypsum—*Zeits. Krist.*, A, vol. 92, pp. 321-343.

JAMES, H. T. (1929): Britannia Beach map-area, British Columbia—*Geol. Surv. Can.*, Mem. 158.

JONES, J. W. (1932): The Bonnecamp map-area, Gaspé Peninsula—*Quebec Bur. Mines*, Ann. Rep., 1931 C, pp. 41-75.

LANGFORD, G. B. and HANCOX, E. G. (1936): Hypogene anhydrite from McIntyre Mine, Porcupine district, Ontario—*Econ. Geol.*, vol. 31, pp. 600-609.

# ON JOSEITE, GRÜNLINGITE, ORUETITE

By M. A. Peacock
*University of Toronto*

With a chemical analysis by V. B. Meen

Bismuth and tellurium, with or without sulphur and selenium, form a series of physically similar minerals only two of which, tellurbismuth and tetradymite, have been adequately defined. At first undistinguished under the chemical name *Tellurwismuth* (Berzelius, 1823),[1] the name tetradymite (Haidinger, 1831) was given to the twinned rhombohedral mineral from Schubkau, near Schemnitz, Hungary, whose composition, $Bi_2Te_2S$, was established by Wehrle (1830) and Berzelius (1831), and has been amply confirmed by later work (Doelter, 1926, p. 855, analyses 1-23). The name tellurbismuth, in an appropriately restricted sense, was applied by Balch (1863) to a North American mineral resembling tetradymite but containing no sulphur, for which he confirmed the composition $Bi_2Te_3$ already given by five analyses by Genth (1855; in Brush, 1861), and now supported in all by nine analyses (Doelter, 1926, p. 858, analyses 1-9). With clear recognition of the essential difference between the two minerals Balch wrote (1863, p. 101): ". . . the American tertellurid of bismuth should be considered a new species, to which the term tetradymite is hardly applicable," thus establishing an entirely appropriate nomenclature. Dana (1892) and others continued, however, to regard tellurbismuth as a sulphur-free variety of tetradymite, for which the composition $Bi_2(Te,S)_3$ was given, and thus the distinction established by Balch has been generally neglected.

Recently the necessity for treating tetradymite and tellurbismuth as distinct minerals has been emphasized by Lange (1939) who showed that the compounds $Bi_2Te_3$ and $Bi_2Te_2S$ co-exist in the artificial system Bi-Te-S; and by Frondel (1940), who found by *x*-ray examination that material from Boliden, Sweden, is an intergrowth of tellurbismuth and tetradymite. Since the two

---

[1] References 1823-1831 taken from Dana (1892, p. 39).

substances can co-exist in the laboratory and in nature without forming intermediate compounds, they cannot be referred to one species with the formula $Bi_2(Te,S)_3$. The writer's recent independent observations on tellurbismuth and tetradymite (Peacock and Berry, 1940, p. 67) are in accord with this conclusion and with the substance of Frondel's able summary of the properties of tellurbismuth.[2]

In addition to tellurbismuth (Bi 52.2 per cent) and tetradymite (Bi 59.2 per cent), one or more minerals of similar appearance, but with Bi 79-83 per cent, have been described from several localities. A mineral from San José, near Mariana, Minas Geraes, Brazil, was described by Damour (1845) whose two analyses suggest the composition[3] $Bi_3TeS$; this mineral was named joseite by Kenngott (1853). A later analysis by Genth (1886), on material from the same locality, gave similar values. More recently Mingaye (1916) has referred a mineral from New South Wales to joseite on the basis of a comparable analysis. A similar mineral from Cumberland, placed close to joseite on the basis of an incomplete analysis by Rammelsberg (1853) was re-examined by Muthmann and Schröder (1898) and named *grünlingite* from two analyses leading to the composition $Bi_4TeS_3$. Still another closely related mineral, from the Serranía de Ronda, Malaga, Spain, was named *oruetite* by Piña de Rúbies (1919), with the composition $Bi_8TeS_4$ derived from the mean of seven analyses of inhomogeneous material. To complete the list of ill-defined bismuth tellurides the *wehrlite* of Huot (1841) may be mentioned; the three available analyses, on material from Deutsch-Pilsen, differ widely and cannot be reduced to a common formula.

---

[2] In this definitive description Frondel adopts the name *tellurobismuthite* (also mis-spelt *telluro-bismutite* in the literature). It would be better to discontinue the use of this superfluous name (Wherry, 1920), with its misleading suggestion of a relation to *bismutite* (*bismuthite*), a powdery basic bismuth carbonate, and retain Balch's previously and properly defined *tellurbismuth*, which aptly suggests an intermetallic compound.

[3] This is the formula derived by Slavík, in Doelter (1926, p. 859). In view of the results obtained in the present work it is interesting to find that Damour himself proposed the formula $Bi_8Te_3S_3$ which, however, accords indifferently with his analyses.

## JOSEITE FROM BRITISH COLUMBIA

In a recent paper Warren and Davis (1940) gave a brief description of joseite and a related telluride, associated with bismuthinite at Glacier Gulch, Hudson Bay Mountain, near Smithers, British Columbia. Taking into account some observations contributed by the present writer, these authors concluded that their material contained joseite (grünlingite), with specific gravity close to 8.0, and a related, possibly new, mineral which gave the composition $Bi_4TeS_2$, from an analysis (Bi 79.3, Te 12.2, S 6.0 = 97.5) on fragments "believed to have an average specific gravity of 8.6."

Since one of the specimens furnished by Dr. Warren showed abundant native bismuth (G = 9.8), and the specific gravity of the analysed fragments varied considerably, the homogeneity of the material with the composition $Bi_4TeS_2$ was doubtful. The repeated identification of joseite in another specimen sent by Dr. Warren, by *x*-ray powder photographs, suggested that the analysed sample was substantially joseite, and that further study of this material might add to the knowledge of this species and bring some clarification among the related minerals. Fortunately some superior material, obtained from Glacier Gulch by Dr. T. L. Walker in 1933, was found in the Royal Ontario Museum and made available for this purpose.

### *Material*

The specimens brought together for this work are listed below:

No. 1.—Joseite (Royal Ontario Museum, M/19602 a), Glacier Gulch, Hudson Bay Mountain, near Smithers, British Columbia. Plates (up to 5 mm. wide) and flakes in parallel orientation, penetrating decomposed rock.

No. 2.—Joseite and native bismuth (Royal Ontario Museum, M/19602 b), same locality. A more continuous tabular mass (6 cm. long) in parallel intergrowth with bismuth, in less abundant gangue.

No. 3.—Joseite ("auriferous tetradymite," Royal Ontario Museum, M/17255), Glacier Gulch, Smithers, British Columbia. Two thick plates (up to 15 mm. wide) with iridescent tarnish and very little attached gangue.

No. 4.—Joseite ("auriferous tetradymite," Royal Ontario Museum, M/19108), Precambrian Mine, Vernon, British Columbia. A rudely tetrahedral mass (40 mm.) of the untarnished mineral, with visible spongy gold and attached calcite.

No. 5.—Joseite (United States National Museum, R 400), San José, Minas

Geraes, Brazil ("type from the collection of A. Damour"). A thin flake (10 mm. wide) with iron-black tarnish.

No. 6.—Joseite (Harvard Mineralogical Museum, 94935), Minas Geraes, Brazil ("material analysed by Genth, 1885"). A thin sheet (30 mm. long) with steely tarnish.

No. 7.—Grünlingite (United States National Museum, C 277), Carrock Fells, Cumberland, England (type locality). A thin blade (20 mm. long) with steely tarnish and some attached bismuthinite, embedded in vein quartz.

No. 8.—Oruetite (United States National Museum, R 7242), Serranía de Ronda, Malaga, Spain (type locality). Several detached tablets (up to 5 mm. wide) with lead-gray tarnish.

The materials Nos. 1 and 2, donated by Dr. Warren, and Nos. 3 and 4, obtained by Dr. Walker, were kindly placed at my disposal by Professor Parsons. Nos. 5, 7, 8, representing valuable type specimens, were courteously lent on the recommendation of Dr. Foshag. Dr. Frondel kindly supplied No. 6.

### *Physical Properties*

Joseite forms sheets or plates without straight outlines, rarely broad blades or tablets showing occasional straight edges, with a foliated structure due to a perfect and exceedingly easy cleavage parallel to the plane of the sheets. Newly separated sheets are galena-white, inclining to silver-white, with high metallic lustre; the folia are soft, flexible, inelastic, and sectile. Old surfaces are lead-gray or tarnished iridescent, steel-blue, to iron-black.

Specific gravity measurements (Berman balance) were made on the available materials, using compact plates (10-20 mg.) cut out with sharp scissors, to give smooth sheared edges. The values given below represent the averages of several determinations with a range of ±0.05.

Except for the inhomogeneous specimens, Nos. 4 and 6, the new values for joseite, grünlingite, and oruetite are practically alike, the observed variation, 8.03-8.15, hardly exceeding the probable error. Joseite (No. 2) gave values ranging from 8 to 9, evidently due to intergrown bismuth. The older values are all lower and very variable, suggesting experimental errors due to the occlusion of air in the ragged edges of the natural mineral plates. With careful measurements it will be possible to distinguish joseite ($G = 8.0$ and over) from tellurbismuth ($G = 7.80$-

7.83, meas; 7.86, calc.) and from tetradymite (G=7.0-7.6, meas.;[4] 7.19, calc.).

Polished sections were made from a clean, thick plate from joseite No. 3, from which the material used for chemical analysis was also obtained. One section was cut nearly parallel to the cleavage, the other nearly perpendicular to the cleavage. In both sections the mineral is homogeneous and free from inclusions. The colour is slightly whiter than galena (A, silver-galena, of Short, 1940, p. 62). The basal section is nearly isotropic; the transverse section is moderately anisotropic, light greenish gray to dark greenish gray. The hardness, estimated by trailing a needle across the sections without pressure on the handle, is noticeably different on the two sections: on the basal section, B (galena); on the transverse section A (argentite). Etch reactions: $HNO_3$, effervesces

TABLE 1

JOSEITE, GRÜNLINGITE, ORUETITE
SPECIFIC GRAVITIES

| | | |
|---|---|---|
| *Joseite* | | |
| British Columbia (Nos. 1, 3) | 8.10 | |
| British Columbia (No. 4)* | 8.2 | |
| Brazil (No. 5) | 8.03 | |
| Brazil (No. 6)* | 8.3 | |
| Brazil | 7.924<br>7.936 | (Dufrenoy)† |
| Brazil | 8.00 | (Hausmann)† |
| New South Wales | 7.688<br>7.793 | (Mingaye, 1916) |
| *Grünlingite* | | |
| Cumberland (No. 7) | 8.15 | |
| Cumberland | 7.321 | (Muthmann and Schröder, 1898) |
| *Oruetite* | | |
| Spain (No. 7) | 8.11 | |
| Spain | 7.6 | (Piña de Rúbies, 1919) |

*These values are given only to the first decimal, since the materials were found, by *x*-rays, to consist of more than one phase.

†In Hintze (1904, p. 408).

---

[4] This variation is surely fictitious; a re-determination on crystals from Schubkau is desirable.

and quickly etches dark gray; fumes tarnish iridescent; HCl, stains light gray; KCN, negative; $FeCl_3$, stains pale blue-gray; KOH, negative; $HgCl_2$, negative. These observations differ only slightly from those of Larsen III (in Frondel, 1940), and confirm the latter's opinion that tellurbismuth, tetradymite, joseite, and grünlingite will not be distinguished with certainty in polished sections.

### *Geometrical Crystallography*

The available material shows some meagre evidence of crystal form, which can be interpreted in terms of the geometrical form of the rhombohedral structural lattice found by the $x$-ray measurements:[5]

$$\alpha = 18°08'; \; a_0 : c_0 = 1 : 9.361$$

The lattice cell (Fig. 1) is thus a very acute rhombohedron, like those of tellurbismuth and tetradymite (Peacock and Berry, 1940), but with an even smaller axial angle. According to the Law of Bravais the most important crystal face and the probable cleavage will follow the most widely spaced (densest) lattice planes. In joseite the spacing of the basal planes (111)(0003) is more than three times as great as that of any other set of lattice planes; this explains the extreme platy habit and facile cleavage parallel to the base. The greater hardness on the base, as compared with the hardness on a transverse section, may also be connected with the extreme relative reticular density of the basal lattice planes.

A few very poor edge-faces were observed and measured on the reflecting goniometer. A small isolated tablet from joseite No. 1, subsequently used for single crystal $x$-ray measurements, showed such a face meeting the base in an edge which proved to be $[1\bar{1}00]$. The measured angle $64 \pm 1°$ compares with the calculated angle, $(111) : (432) = (0003) : (1\bar{1}29) = 64°19\frac{1}{2}'$. Another tablet, from joseite No. 2, showed a similar facet measuring $86 \pm 1°$, which is comparable to the calculated angle, $(111) : (100) = (0003) : (10\bar{1}1)$

---

[5] Since the lattice of joseite is rhombohedral the crystallography, geometrical and structural, is properly described in rhombohedral notation. On the other hand the hexagonal notation is more convenient in actual practice and is used exclusively by many authors. Dual notation will therefore be used throughout, as in the description of ungemachite (1938), which is prefaced by a concise explanation of the relations of the two notations.

=84°43′. A symmetrically developed crystal *cr* would thus look like the six-sided plate shown in Fig. 1.

Joseite No. 3 showed several cases of apparently regular intergrowth of two individuals with basal planes meeting at a low angle. In view of the twinning known in tetradymite several of these angles were measured. Four fair measurements gave 16°52′—17°02′; but as these do not correspond to any simple twinning operation the intergrowths appear to be of a random nature.

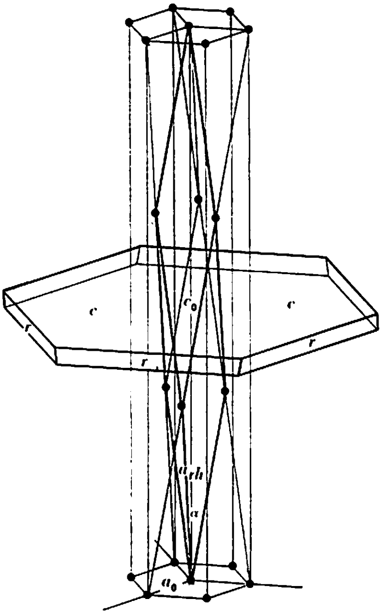


FIG. 1.—Joseite, Glacier Gulch, B.C. (No. 1): the rhombohedral structural lattice inscribed in a symmetrically developed crystal *cr*, showing the large spacing of the basal lattice planes in relation to the platy habit.

### *Structural Crystallography*

In spite of the unfavourable nature of the material it was found possible to make useful *x*-ray photographs both with powders and with single crystals. The previously mentioned tablet from joseite

No. 1 was used for rotation and zero Weissenberg photographs about the hexagonal axes [0001] and [$1\bar{1}00$]. Sharp records of the basal diffractions alone were obtained from several of the other materials, by making zero Weissenberg resolutions from small plates (about $1.0 \times 0.2 \times 0.1$ mm.) turning about random axes in the basal plane. Such plates were cut with a razor blade, from thin sheets lying on an object glass, and made quite flat by gentle pressure with a second object glass.

The rotation photograph about the normal to the cleavage [0001] (Fig. 2) shows a large number of rather thinly occupied layer lines ($l=0$—$21$) composed of spots forming more distinct row lines. Due to some crystal imperfection, or lack of perfect adjustment, the spots are also smeared on powder curves. The Weissenberg resolution of the zero layer line (Fig. 3) gives the diffractions ($hk\bar{i}0$). The Weissenberg resolutions of the zero layer line about [$1\bar{1}00$] (Fig. 4) shows the diffractions ($000l$) up to $l=48$, and the diffractions ($hh\overline{2h}l$) up to $l=45$. These films lead to a rhombohedral cell:

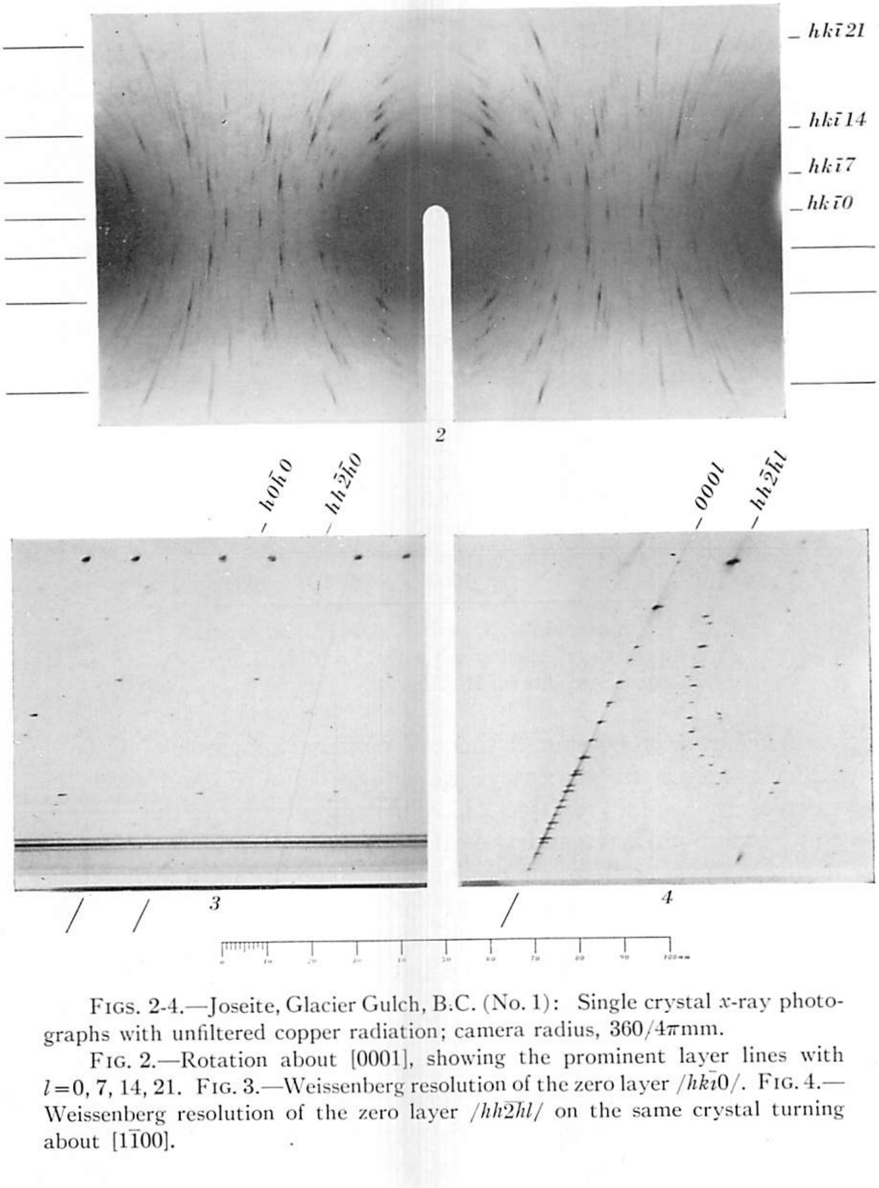
$$a_{rh} = 13.45\,\text{Å};\ \alpha = 18°08'$$

calculated from the measured hexagonal elements:

$$a_0 = 4.24 \pm 0.01\,\text{Å};\ c_0 = 39.69 \pm 0.06\,\text{Å}$$

There are no systematic extinctions beyond the rhombohedral condition $(h+i+l)=3n$; consequently the aspect (Donnay and Harker, 1940) is R**, in which the most symmetrical space group is $D_{3d}^{5} = R\bar{3}m$. The Weissenberg film of the diffractions ($hk\bar{i}0$) shows a few very weak spots that do not conform to the rhombohedral extinction rule. None of these spots is represented in the powder photographs; from the rotation photograph (Fig. 2) they appear to be due to weak continuous diffractions from rhombohedral spots on the closely adjoining layers $l=1$ and $l=\bar{1}$. These faint spots may, however, indicate a weak hexagonal superlattice with the elements given above and three times the rhombohedral cell content.

From the volume of the rhombohedral cell ($V=206.0$ Å$^3$) and the measured specific gravity (G$=8.10$) the molecular weight of the cell content is M$=1012$.



Figs. 2-4.—Joseite, Glacier Gulch, B.C. (No. 1): Single crystal $x$-ray photographs with unfiltered copper radiation; camera radius, $360/4\pi$mm.

Fig. 2.—Rotation about [0001], showing the prominent layer lines with $l=0, 7, 14, 21$. Fig. 3.—Weissenberg resolution of the zero layer $/hk\bar{i}0/$. Fig. 4.—Weissenberg resolution of the zero layer $/hh\overline{2h}l/$ on the same crystal turning about [1$\bar{1}$00].

### *Composition and Cell Content*

A sample of joseite No. 3 was prepared for chemical analysis, using a part of the tablet which gave the previously described polished sections. Specific gravity measurements and *x*-ray powder photographs showed that the sample was identical with the material used for single crystal measurements. A microanalysis by Dr. Meen, representing duplicate determinations of each constituent on separate samples of 16-20 mg., gave the values in column 1, Table 2.

TABLE 2

JOSEITE FROM BRITISH COLUMBIA
ANALYSIS AND CELL CONTENT

| | 1 | 2 | 3 |
|---|---|---|---|
| Bi | 82.7 | 3.98 | 81.4 |
| Te | 12.0 | 0.95 | 12.4 |
| S | 6.0 | 1.88 | 6.2 |
| Se | none | ... | ... |
| | 100.7 | 6.81 | 100.0 |

1. Material No. 3, anal. V. B. Meen. 2. Atoms in the rhombohedral cell with $M = 1012$. 3. Percentage weights for $Bi_4TeS_2$.

As shown in column 2 the cell content approaches $Bi_4TeS_2$, which requires the percentage weights in column 3 and gives the calculated specific gravity 8.23. This composition is the same as that given by Warren and Davis (1940) for material from the same locality, showing that our observations refer to substantially the same material. The confirmed formula differs from all those mentioned in the review of previously described bismuth tellurides.[6]

In spite of the shortage in Te and S, the ideal number of atoms in the rhombohedral cell is clearly seven. Tellurbismuth ($Bi_2Te_3$) and tetradymite ($Bi_2Te_2S$) contain five atoms in the rhombohedral cell; these lie on vertical rows, giving a 15-layer structure (Harker, 1934). The natural presumption that joseite has a similar arrangement of seven atoms, giving a 21-layer structure, is supported by a

---

[6] If the new formula is written $Bi_4(Te,S)_3$, as in a recent abstract (1940), we have correspondence with the formula $Bi_8Te_3S_3$ suggested by Damour (1845).

rough estimate of the resulting length of the vertical period. If the layers are spaced as in tetradymite the joseite structure would have $c_0 = 38.1$ Å, which is comparable to the observed value, 39.7 Å. The presumed kind of arrangement is also indicated by the fact that most of the strong diffractions have *l*-indices (hexagonal notation) which are divisible by seven (Table 3).

### *Powder Spectrum*

The *x*-ray powder spectrum given by several samples of joseite Nos. 1 and 3, with nickel-filtered copper radiation, is reproduced in Fig. 9. This pattern, like those given for comparison, is somewhat diffuse. Lack of sharpness might be related to deformation in grinding. However the degree of diffusion is constant in all the joseite patterns and no greater than that shown in the rotation photograph, whereas the patterns from well-crystallized tetradymite and tellurbismuth, with exact compositions and similar physical properties, are somewhat sharper. This suggests that the diffusion is due to structural imperfection rather than mechanical deformation.

To provide a reliable means of identifying this mineral, and to show that none of the samples that gave this pattern contained any considerable amount of other material, the spectrum has been completely indexed and all the lines but two have been identified with single crystal diffractions of appropriate intensity. The two lines in question correspond to indices that lay beyond the range of the single crystal photographs.

## JOSEITE FROM BRAZIL; GRÜNLINGITE; ORUETITE

### *Structural Comparison*

Our specimens of joseite from San José (described as Damour's type, No. 5), grünlingite from Carrock Fells (No. 7), and oruetite from Serranía de Ronda (No. 8) give *x*-ray powder patterns which are alike and are the same as that of the mineral from Glacier Gulch (Figs. 8-11). Measurements from the four films show that joseite No. 5 has a slightly smaller cell than that of the others, indicating slight chemical variation within a fixed structural type.

### TABLE 3

### JOSEITE FROM BRITISH COLUMBIA
### POWDER SPECTRUM WITH Cu-$K\alpha$ RADIATION

$a_{rh} = 13.45\,\text{Å},\ \alpha = 18°08'$; $a_o = 4.24\,\text{Å},\ c_o = 39.69\,\text{Å}$

| *I*(P) | *d*(meas.) | *hkl* | *hkīl* | *d*(calc.) | *I*(S) |
|---|---|---|---|---|---|
| m | 4.38 | (333) | (0009) | 4.41 | s |
| m | 3.61 | (110) | $(01\bar{1}2)$ | 3.61 | * |
| vw($\beta$) | 3.09 | (322) | $(10\bar{1}7)$ | 3.08 | m($\beta$) |
| w | 3.30 | (444) | (0.0.0.12) | 3.31 | s |
| vvs | 3.07 | (322) | $(10\bar{1}7)$ | 3.08 | vs |
| m | 2.57 | (443) | $(0.1.\bar{1}.11)$ | 2.57 | m |
| s | 2.24 | (554) | $(0.1.\bar{1}.14)$ | 2.24 | vs |
| s | 2.11 | $(10\bar{1})$ | $(11\bar{2}0)$ | 2.12 | m |
| w | 2.05 | (655) | $(1.0.\bar{1}.16)$ | 2.06 | m |
| w | 1.967 | (665) | $(0.1.\bar{1}.17)$ | 1.970 | s |
| m | 1.894 | (777) | (0.0.0.21) | 1.890 | s |
| vw | 1.819 | (766) | $(1.0.\bar{1}.19)$ | 1.816 | m |
| vw | 1.779 | (543) | $(1.1.\bar{2}.12)$ | 1.785 | m |
| m | 1.744 | (331) | $(02\bar{2}7)$ | 1.747 | s |
| w | 1.654 | (888) | (0.0.0.24) | 1.654 | s |
| vw | 1.616 | (877) | $(1.0.\bar{1}.22)$ | 1.619 | – |
| m | 1.537 | (644) | $(2.0.\bar{2}.14)$ | 1.541 | s |
| m | 1.409 | (876) | $(1.1.\bar{2}.21)$ | 1.411 | s |
| m | 1.345 | (421) | $(21\bar{3}7)$ | 1.348 | s |
| w | 1.302 | (987) | $(1.1.\bar{2}.24)$ | 1.304 | m |
| m | 1.246 | (653) | $(1.2.\bar{3}.14)$ | 1.247 | s |
| vw | 1.221 | $(2\bar{1}\bar{1})$ | $(30\bar{3}0)$ | 1.224 | s |
| m | 1.210 | (754) | $(2.1.\bar{3}.16)$ | 1.211 | m |
| vw | 1.176 | (522) | $(30\bar{3}9)$ | 1.179 | m |
| vw | 1.044 | (12.11.10) | $(1.1.\bar{2}.33)$ | 1.046 | m |
| w | 1.026 | (966) | $(3.0.\bar{3}.21)$ | 1.027 | s |
| m | 1.005 | (430) | $(13\bar{4}7)$ | 1.002 | s |
| w | 0.982 | (13.12.11) | $(1.1.\bar{2}.36)$ | 0.978 | s |
| w | 0.956 | (743) | $(3.1.\bar{4}.14)$ | 0.958 | s |
| w | 0.943 | (11.8.8) | $(3.0.\bar{3}.27)$ | 0.941 | – |
|  |  | (12.10.9) | $(2.1.\bar{3}.31)$ | 0.941 | – |
| m | 0.907 | (511) | $(40\bar{4}7)$ | 0.906 | s |
| m | 0.836 | (520) | $(32\bar{5}7)$ | 0.833 | s |
| m | 0.816 | (16.15.14) | $(1.1.\bar{2}.45)$ | 0.814 | vs |

*I*(P)—intensity of powder ring; *d*(meas.)—measured spacing; (*hkl*)—rhombohedral indices; (*hkīl*)—hexagonal indices; *d*(calc.)—calculated spacing; *I*(S)—intensity of single crystal diffraction, if in the range of photographs taken. *—Concealed by central blackening on rotation photograph.

These particular specimens thus represent a single species with essentially the properties given for the mineral from Glacier Gulch. If the authenticity of our materials can be relied upon, joseite, grünlingite, and oruetite should be united under the earliest adequately defined name, joseite, and the mineral from Glacier Gulch should be referred to this species.

This provisional conclusion is partly, but not wholly, in agreement with recent observations on bismuth tellurides. Garrido and Feo (1938) obtained practically identical *x*-ray powder photographs for grünlingite (Cumberland) and oruetite (Spain), on material in the National Museum of Natural History in Paris. From this it is concluded that grünlingite and oruetite are substantially alike. This result was confirmed by Frondel on specimens in the Harvard Mineralogical Museum. Garrido and Feo's nearly identical lists of powder spacings and intensities for grünlingite and oruetite are also closely comparable to those given in Table 3. On the other hand Garrido and Feo obtained a distinctly different list of spacings and intensities from a specimen of joseite from Brazil. Frondel likewise obtained different patterns from joseite and grünlingite.[7] Different specimens from Brazil are thus evidently not alike and it appears unsafe to accept our specimen (No. 5) as type material.

This uncertainty regarding the authenticity of our specimen of joseite (No. 5) from Brazil led to a search for further material. Two specimens, joseite from Brazil (No. 6), and joseite from Vernon, British Columbia (No. 4), yielded interesting results which will be briefly stated here.[8]

The powder photograph of joseite (No. 6, Fig. 12), representing the material analysed by Genth (1886), is similar to the foregoing patterns but markedly contracted, indicating a similar structure with larger cell dimensions. This pattern was fully indexed by analogy with the previously indexed pattern, giving the lattice elements:

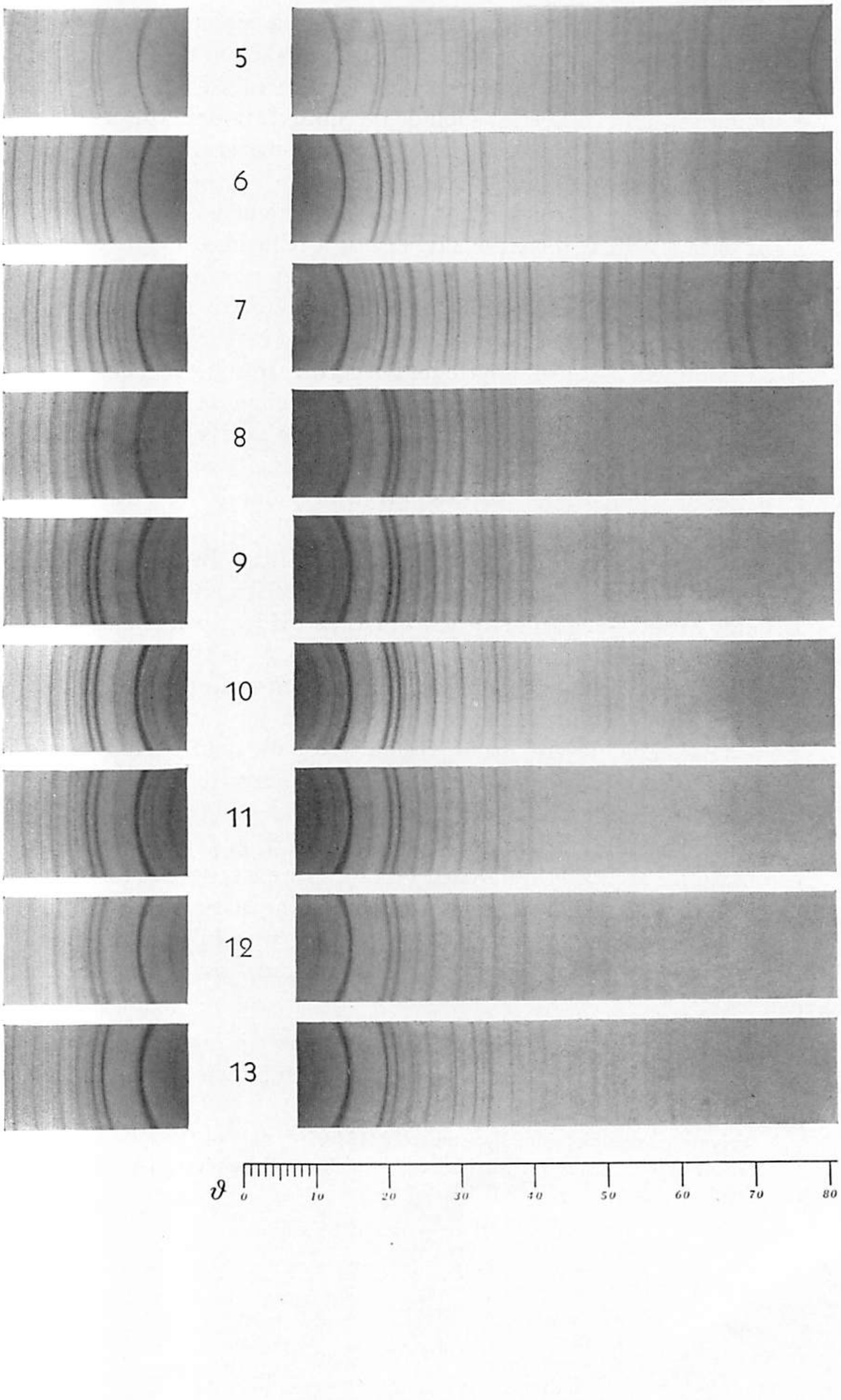
$$a_{rh} = 13.81\text{ Å},\ \alpha = 18°02';\ a_0 = 4.33,\ c_0 = 40.75\text{ Å};\ V_{rh} = 220.6\text{ Å}^3$$

as compared with the values given by the previously described materials:

---

[7] Private communication, November 19, 1940.

[8] These specimens require further study which may be undertaken on another occasion.


5
6
7
8
9
10
11
12
13
ϑ
0
10
20
30
40
50
60
70
80

$a_{rh} = 13.45$ Å, $\alpha = 18°08'$; $a_0 = 4.24$, $c_0 = 39.69$ Å; $V_{rh} = 206.0$ Å$^3$

The list of spacings and intensities from our joseite (No. 6) does not, however, agree with that of Garrido and Feo.

Joseite from Vernon, British Columbia (No. 4) also gave a pattern (Fig. 13) of similar type, showing further contraction corresponding to still larger cell dimensions:

$a_{rh} = 14.26$ Å, $\alpha = 17°47\frac{1}{2}'$; $a_0 = 4.41$, $c_0 = 42.09$ Å; $V_{rh} = 236.3$ Å$^3$

The spacings and intensities from this material agree with those given for joseite from Brazil by Garrido and Feo. It thus appears that different specimens of joseite from Brazil show a general structural similarity, but vary in cell dimensions, with an observed variation of nearly 15 per cent in cell volume. Such variation in an isostructural series or group indicates considerable variation in chemical composition.

FIGS. 5-13.—Bismuth and bismuth tellurides: *x*-ray powder photographs with copper radiation (nickel filter); camera radius, 360/4π mm.; reversed prints reproduced full size.

FIG. 5.—Native bismuth, Cobalt, Ontario. FIG. 6.—Tellurbismuth (artificial); identical photographs were obtained from natural tellurbismuth (Peacock and Berry, 1940, p. 67). FIG. 7.—Tetradymite (crystallized), Schubkau, Hungary. FIG. 8.—Joseite, Brazil (No. 5). FIG. 9.—Joseite, Glacier Gulch, B.C. (No. 3). FIG. 10.—Grünlingite, Cumberland (No. 7). FIG. 11.—Oruetite, Spain (No. 8). FIG. 12.—Joseite, Brazil (No. 6). FIG. 13.—Joseite, Vernon, B.C. (No. 4).

Records of the basal diffractions, from zero Weissenberg resolutions on plates turning about random axes in the basal plane, with filtered radiation (Fig. 14), revealed further complications. Such photographs from joseite No. 3 (British Columbia) and joseite No. 5 (Brazil) are strictly comparable, giving single series of diffractions with the intensities and spacings in Table 4. Joseite No. 6 (Brazil) gave a double series, with different intensity sequences and different spacings, the same surprising effect being obtained from a second plate. This material from Brazil is thus composed of two similar but distinct phases, A and B, in parallel intergrowth. These phases have different sequences of intensity but similar basal spacings, 13.50 and 13.74 Å, respectively; the mean basal spacing, 13.62 Å, is close to 13.58 Å obtained from the powder photograph, which evidently does not differentiate the two components.

The basal diffractions from a plate of joseite No. 4 (British

Columbia) showed the presence of two or even more phases in parallel intergrowth, all with different sequences of intensity and similar spacings, and all different from the phases in joseite No. 6. One of these phases is much more abundant than the others, being mainly responsible for the lines on the powder diagram which yielded the cell elements given above.

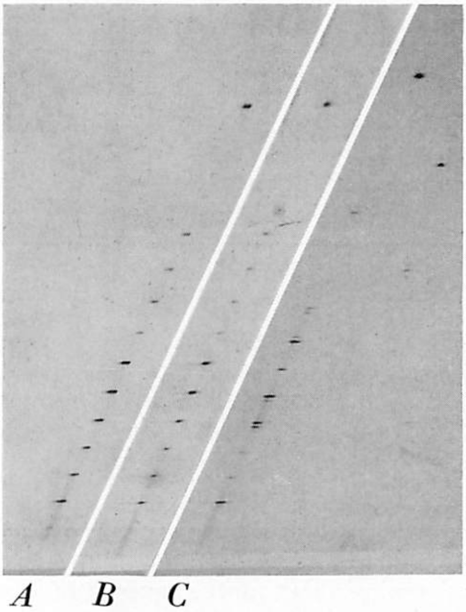


FIG. 14.—Basal diffractions (*hhh*) from Weissenberg resolutions on plates turning about random axes in the basal plane (copper radiation, nickel filter): *A*—Joseite, Glacier Gulch (No. 3); *B*—Joseite, Brazil (No. 5); *C*—Joseite, Brazil (No. 6), showing two phases, neither of which is identical with that in *A* and *B*.

The detailed study of the several similar but distinct phases found in specimens of joseite Nos. 4 and 6 is beyond the scope of the present work. It may be noted, however, that the dominant phase in each of the plates examined gives a strong diffraction for the seventh order of the basal planes (777)(0.0.0.21), indicating a 7-atom cell and a 21-layer structure, as inferred for the homogeneous joseite. The progressive expansion of the dominant phase points to chemical variation in a 7-atom cell with increase in the proportion

TABLE 4

JOSEITE: OBSERVED INTENSITIES AND SPACINGS OF BASAL DIFFRACTIONS (*hhh*)

| British Columbia (No. 3) and Brazil (No. 5) | | | Brazil (No. 6) | | | |
|---|---|---|---|---|---|---|
| | | | A | | B | |
| *h* | *I** | $d_{111}$ | *I* | $d_{111}$ | *I* | $d_{111}$ |
| 1 | w | 12.96 | — | — | — | — |
| 2 | w | 13.08 | vw | 13.54 | — | — |
| 3 | s | 13.28 | s | 13.45 | — | — |
| 4 | s | 13.17 | — | — | m | 13.69 |
| 5 | m | 13.22 | — | — | w | 13.78 |
| 6 | s | 13.23 | s | 13.48 | ms | 13.85 |
| 7 | s | 13.25 | vs | 13.57 | m | 13.91 |
| 8 | s | 13.25 | — | — | ms | 13.68 |
| 9 | w | 13.22 | w | 13.46 | s | 13.72 |
| 10 | m | 13.25 | m | 13.52 | w | 13.75 |
| 11 | w | 13.22 | — | — | — | — |
| 12 | m | 13.23 | — | — | — | — |
| 13 | w | 13.21 | vw | 13.50 | ms | 13.65 |
| 14 | vw | 13.21 | — | — | — | — |
| 15 | vs | 13.23 | — | — | — | — |
| 16 | vw | 13.25 | — | — | s | 13.63 |
| Average $d_{111}$ | | 13.23 Å | | 13.50 Å | | 13.74 Å |

*This sequence of intensities was taken from the more strongly exposed photograph, Fig. 4.

of the largest atom (Bi) up to and beyond the limit of stability, when further chemical variation gives rise to distinct subsidiary phases.

To determine the cell content of the Brazilian joseite Damour's two analyses cannot be used directly, since we have no assurance that any of the material examined corresponds to that analysed. On the other hand, Genth's analysis may be used, with the cell volume and specific gravity determined on the analysed material, to obtain the approximate cell content of the dominant phase.

The content of the unit cell approaches a sum of 7 atoms, with Bi substantially in excess of 4 and (Te+Se+S) considerably short of 3. This excess of Bi, the largest atom, at the expense of (Te+Se+S), is in keeping with the increased size and specific gravity of the unit cell of the principal phase; the presence of a distinct subordinate phase indicates that the excess of Bi is greater than the amount tolerated by the phase $Bi_4(Te,Se,S)_3$.

TABLE 5

JOSEITE (NO. 6) FROM BRAZIL
ANALYSIS AND CELL CONTENT

| | 1 | 2 | 3 |
|---|---|---|---|
| Bi | 81.23 | 4.31 | 4.45 |
| Te | 14.67 | 1.27 | 1.32 |
| Se | 1.46 | 0.20 | 0.21 |
| S | 2.84 | 0.98 | 1.02 |
| | 100.20 | 6.76 | 7.00 |

1. Anal. Genth (1886). 2. Atoms in rhombohedral cell with $V_0 = 220.6$ Å$^3$, $G = 8.3$. 3. Content of a 7-atom cell.

The foregoing structural comparison has revealed the identity of single specimens from Glacier Gulch, British Columbia (joseite), Brazil (joseite), Cumberland (grünlingite), and Spain (oruetite). This mineral is also identical with the specimens of grünlingite and oruetite examined by Garrido and Feo, and by Frondel. The Canadian example is homogeneous, and has a rhombohedral cell containing very nearly $Bi_4TeS_2$, or more generally $Bi_4(Te,S)_3$. These specimens are therefore referable to one species whose composition must be nearly constant. Another specimen from Brazil, composed of two similar phases, gave a larger cell containing $Bi_{4.45}(Te,Se,S)_{2.55}$ in a 7-atom cell. A specimen from Vernon, British Columbia, showed two or more phases and gave a powder diagram which agrees with that obtained on joseite from Brazil by Garrido and Feo, and yields a still larger unit cell.

### *Chemical Considerations*

The wide variation in existing analyses of joseite and the allied minerals appears to be due to extensive mutual substitution in a 7-atom cell. We may therefore reduce the relevant analyses to the form (Bi+Te+Se+S)=7 atoms to exhibit the variation of cell content (Table 6).

TABLE 6

Joseite, Grünlingite, Oruetite
Analyses Reduced to (Bi+Te+Se+S)=7 Atoms

| Anal. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Bi | 78.82 | 79.31 | 79.3 | 82.7 | 82.92 | 79.15 | 78.40 | 86.78 | 83.30 | 81.23 |
| Te | 12.66 | 12.82 | 12.2 | 12.0 | 9.16 | 15.93 | 15.68 | 6.35 | 6.65 | 14.67 |
| Se | .... | .... | none | none | trace | 1.48 | 1.47 | .... | .... | 1.46 |
| S | 9.40 | 9.31 | 6.0 | 6.0 | 6.19 | 3.15 | 3.11 | 6.84 | 6.35 | 2.84 |
| | 100.88 | 101.44 | 97.5 | 100.7 | 99.83 | 99.71 | 98.66 | 99.97 | 97.52 | 100.20 |
| Atoms | | | | | | | | | | |
| Bi | 3.43 | 3.45 | 4.01 | 4.09 | 4.20 | 4.27 | 4.28 | 4.29 | 4.30 | 4.45 |
| Te | 0.90 | 0.91 | 1.01 | 0.97 | 0.76 | 1.41 | 1.40 | 0.51 | 0.56 | 1.32 |
| Se | .... | .... | .... | .... | .... | 0.21 | 0.21 | .... | .... | 0.21 |
| S | 2.67 | 2.64 | 1.98 | 1.94 | 2.04 | 1.11 | 1.11 | 2.20 | 2.14 | 1.02 |

1, 2. Grünlingite, Cumberland; anal. Muthmann and Schröder (1898).

3. Joseite or a related mineral, Glacier Gulch, Hudson Bay Mountain, near Smithers, B.C.; anal. Forward, in Warren and Davis (1940).

4. Joseite, Glacier Gulch, Smithers, B.C. (No. 3); anal. Meen.

5. Joseite, Whipstick Mine, New South Wales; anal. Mingaye (1916). Total includes Mn 0.77, Fe 0.47, insol. 0.32.

6, 7. Joseite, San José, Minas Geraes, Brazil; anal. Damour (1845). In anal. 7, in which the combined value Se+S=4.58 was reported, the value Se 1.47 is assumed on the basis of reported values in anal. 6 and 10.

8. Oruetite, Serranía de Ronda, Malaga, Spain; anal. Piña de Rúbies (1919).

9. Joseite, Carrock Fells, Cumberland; anal. Rammelsberg (1853). Total includes quartz 1.22.

10. Joseite, Minas Geraes, Brazil; anal. Genth (1886).

Disregarding for the moment analyses 1 and 2 ("grünlingite") it will be seen that the number of Bi-atoms per unit cell varies from 4.01-4.09 in the Canadian type to 4.45 in Genth's material from Brazil. This increase in Bi-atoms, which are much larger than the atoms of Te, Se, or S, would cause the observed increase in cell volume and density. The fact that Piña de Rúbies' mineral (anal. 8) was inhomogeneous and Genth's mineral (anal. 10) showed two structural phases, indicates that the limiting amount of Bi in homogeneous joseite is about 4.3 atoms per unit cell. Mutual substitution to this extent is not uncommon in minerals of metallic character, and it is in keeping with the range of stability of single phases in comparable artificial systems. We may therefore write the following general structural formula for joseite in the wide sense:

$$Bi_{4+x}(Te,Se,S)_{3-x}$$

where $x$ is 0-0.3.

Looking to the values for Te, Se, S, again leaving aside analyses 1 and 2, we find that the number of S-atoms per unit cell is either nearly 2 (average 2.06) or nearly 1 (average 1.08); the former composition is given by material from British Columbia, New South Wales, Spain, and Cumberland; the latter is confined to material from Brazil. Se, reported only from Brazil, is evidently structurally equivalent to Te.[9] There is thus chemical evidence for two types of joseite, with the structural formulas:

$$Bi_{4+x}Te_{1-x}S_2$$
$$Bi_{4+x}(Te,Se)_{2-x}S$$

These formulas express a chemical difference comparable to that which distinguishes tellurbismuth and tetradymite; however, it cannot be said that the difference is specific until the second formula has been confirmed on homogeneous material.

The interpretation of Muthmann and Schröder's analysis of grünlingite (1 and 2) presents special difficulties. It does not seem possible that these analyses represent the specimens of grünlingite examined by Garrido and Feo (1938), Frondel, and the present writer. Perhaps none of the specimens examined by $x$-rays was authentic; on the other hand the analysed material might not have been homogeneous, in spite of careful preparation and inspection. In this connection it is noteworthy that grünlingite is often intergrown with bismuthinite; one of our specimens labelled grünlingite proved to be wholly bismuthinite. Some mixtures of joseite and bismuthinite would give the composition attributed to grünlingite. If further work on material from Cumberland fails to confirm the

---

[9] All the materials used in the present study were tested for selenium, using the stannous chloride test and the open tube. The wet test proved unsatisfactory in presence of abundant tellurium; the dry test showed selenium present in the two specimens from Brazil, absent in the others.

high sulphur in grünlingite this name and the implied composition may be discarded.

## SUMMARY

Joseite from Glacier Gulch, near Smithers, British Columbia, is rhombohedral with $\alpha = 18°08'$, $a_o : c_o = 1 : 9.361$ (from $x$-ray measurements). Forms (111)(0003), the plane of sheet-like development; uncertain $(100)(10\bar{1}1)$, (432)(1129). Space-group $D_{3d}^5 = R3m$. Cell dimensions $a_{rh} = 13.45$ Å, $\alpha = 18°08'$ (from the hexagonal values $a_o = 4.24 \pm 0.01$ Å, $c_o = 39.69 \pm 0.06$ Å). Cleavage (111)(0003), perfect and easy, giving flexible folia. Hardness B on the base, A across the folia. Specific gravity 8.10. Galena-white, moderately anisotropic; not distinguished from tetradymite in polished sections. Microanalysis (V. B. Meen): Bi 82.7, Te 12.0, S 6.0, Se none = 100.7, giving the composition $Bi_4TeS_2$, which is also the rhombohedral cell content. The $x$-ray photographs indicate a 21-layer structure analogous with the 15-layer structure of tetradymite.

The fully indexed $x$-ray powder photograph is identical with powder photographs of grünlingite (G = 8.15) from Cumberland, and oruetite (G = 8.11) from Spain. One specimen of joseite (G = 8.03) from Brazil gives a similar pattern with a slightly smaller cell. Another specimen of joseite (G = 8.3) from Brazil gives a distinctly larger cell, $a_{rh} = 13.81$ Å, $\alpha = 18°02'$, (from $a_o = 4.33$ Å, $c_o = 40.75$ Å). A specimen of joseite (G = 8.2) from Vernon, British Columbia, gives a still larger cell, $a_{rh} = 14.26$ Å, $\alpha = 17°47\frac{1}{2}'$ (from $a_o = 4.41$ Å, $c_o = 42.09$ Å). The pattern from this mineral agrees with the powder data for joseite given by Garrido and Feo. Both these materials with larger cells contain additional phases, as shown by the basal diffractions from single plates.

The relevant analyses are reduced to (Bi + Te + Se + S) = 7 atoms, giving a general structural formula for joseite, including grünlingite and oruetite: $Bi_{4+x}(Te,Se,S)_{3-x}$ with $x = 0—0.3$. Variation in $x$ explains the variation in cell dimensions. Within this general formula the analyses indicate two types $Bi_{4+x}Te_{1-x}S_2$ (fully confirmed) and $Bi_{4+x}(Te,Se)_{2-x}S$ (requiring confirmation). Muthmann and Schröder's two analyses of grünlingite are incompatible with the present and previous $x$-ray observations; it is suggested that these analyses may represent intergrowths of joseite and bismuthinite.

## REFERENCES

Balch, D. M. (1863): On tellurbismuth from Dahlonega, Georgia—*Am. Jour. Sci.*, vol. 35, pp. 99-101.

Brush, G. J. (1861): Ninth supplement to Dana's mineralogy—*Am. Jour. Sci.*, vol. 31, pp. 354-371.

Damour, A. (1845): Analyse d'un tellurure de bismuth du Brézil—*Ann. Chim. Phys.*, vol. 13, pp. 372-376.

Dana, E. S. (1892): *System of Mineralogy*, ed. 6—New York.

Doelter, C. (1926): *Handbuch der Mineralchemie*, vol. 4 (1)—Dresden and Leipzig.

Donnay, J. D. H. and Harker, D. (1940): Nouvelles tables d'extinctions pour les 230 groupes de recouvrements cristallographiques—*Naturaliste Canadien*, vol. 67, pp. 33-69.

Frondel, C. (1940): Redefinition of tellurobismuthite and vandiestite—*Am. Jour. Sci.*, vol. 238, pp. 880-888.

Garrido, J. and Feo, R. (1938): Sur les sulfotellurures de bismuth—*Bull. Soc. franç. Min.*, vol. 61, pp. 196-204.

Genth, F. A. (1855): Contributions to mineralogy—*Am. Jour. Sci.*, vol. 19, pp. 15-23.

———— (1886): Contributions from the laboratory of the University of Pennsylvania, no. xxiv, contributions to mineralogy—*Am. Phil. Soc. Philadelphia*, vol. 23, pp. 30-47.

Harker, D. (1934): The crystal structure of the mineral tetradymite—*Zeits. Krist.*, A, vol. 89, pp. 175-181.

Hintze, C. (1904): *Handbuch der Mineralogie*, vol. 1 (1)—Leipzig.

Huot, J. J. N. (1841): *Manuel de Minéralogie*, vol. 1—Paris.

Kenngott, G. A. (1853): *Das Mohs'che Mineralsystem*—Vienna.

Lange, P. W. (1939): *Ein Vergleich gwischen* $Bi_2Te_3$ and $Bi_2Te_2S$—*Naturwiss.*, vol. 27, p. 133.

Mingaye, J. C. H. (1916): Notes from the chemical laboratory—*Rec. Geol. Surv. N.S.W.*, vol. 9, pp. 127-135.

Muthmann, W. and Schröder, E. (1898): Ueber die Zusammensetzung einiger Tellurmineralien—*Zeits. Krist.*, vol. 29, pp. 140-145.

Peacock, M. A. (1941): Joseite from British Columbia (abs.)—*Am. Mineral.*, vol. 26, p. 200.

———— and Bandy, M. C. (1938): Ungemachite and clino-ungemachite: New minerals from Chile—*Am. Mineral.*, vol. 23, pp. 314-328.

———— and Berry, L. G. (1940): Röntgenographic observations on ore minerals—*Univ. Toronto Studies, Geol. Ser.*, no. 44, pp. 47-69.

Pina de Rubies, S. (1919): La oruetita, nuevo sulfotelururo de bismuto—*Anal. Soc. Españ. Fis. Quim.*, vol. 17, pp. 83-87.

Rammelsberg, C. F. (1853): *Handwörterbuch des chemischen Theils der Mineralogie*, Supplement 5—Berlin.

SHORT, M. N. (1940): Microscopic determination of the ore minerals—*U.S. Geol. Surv.*, Bull. 914.

WARREN, H. V. and DAVIS, P. (1940): Some bismuth minerals from British Columbia—*Univ. Toronto Studies, Geol. Ser.*, no. 44, pp. 107-111.

WHERRY, E. T. (1920): The nomenclature and classification of sulfide minerals—*Jour. Washington Acad. Sci.*, vol. 10, pp. 487-496.

# PRECISE MEASUREMENTS OF THE CUBE-EDGE OF COMMON PYRITE AND NICKELIFEROUS PYRITE

By M. A. PEACOCK and F. G. SMITH
*University of Toronto*

In connexion with the problem presented by the remarkable variation in the electrical conductivity of pyrite (Smith, 1940) observations were made on some of the other properties of this mineral in the hope of revealing variations which might be related to the electrical behaviour. Among these observations were measurements on sharp *x*-ray powder films obtained from two samples representing the extreme range of conductivity. These revealed no appreciable difference in the positions or intensities of the lines, the cube-edge being 5.410±0.005 Å, in good agreement with the more exact existing values.

Returning to the pyrite problem the junior author became interested in the possible variation in the cube-edge of common pyrite with variation of composition. To test this possibility an accurate back-reflection powder method was devised and applied to two analysed specimens with the compositions $FeS_{2.00}$ and $FeS_{1.98}$, respectively. Combined with exact specific gravity measurements the cell-edges indicated the nature of the structural imperfection which must exist in the crystal deficient in sulphur. With a suitable method available the opportunity was also taken to remeasure the cell-edge of a nickeliferous pyrite and to decide whether it differs sensibly from the cell-edge of ordinary pyrite.

We have been assisted in this work by the kindness of Professor L. J. Rogers, who analysed one of our samples of pyrite; Professor F. E. Beamish, who made a spectrographic examination of one specimen; Professor H. J. C. Ireton, who gave the use of a travelling microscope; Dr. J. G. Breckenridge, who provided purified carbon tetrachloride; and Messrs. Birks-Ellis-Ryrie, Toronto, who lent us a cut diamond.

## ARRANGEMENT AND CALIBRATION OF THE POWDER CAMERA

Our powder camera, made after the design of Buerger (1936), has the nominal radius 360/4π mm. ($1°\theta = 1$ mm.). Ordinarily the film is fitted so that the $x$-ray beam enters between the ends of the film and leaves through a hole in the middle (Fig. 1a). For exact measurement of the sensitive high-$\theta$ rings (the so-called back-reflection rings) the film may be inserted in the reversed position, in which the $x$-ray beam enters through the central hole and leaves between the ends (Fig. 1b). In this way errors due to film-shrinkage are much reduced since the measurements cover only a short length of film on either side of the pin-hole.

A further marked advantage is gained by arranging the film so that the ends nearly meet midway between the inlet and the outlet of the beam (Fig. 1c). With this arrangement the low-$\theta$ diffraction rings centre on the position $M$ ($\theta = 0°$), the high-$\theta$ rings centre on the opposite position $M'$ ($\theta = 90°$). These positions on a continuous length of film can be fixed with great accuracy, giving the effective semi-circumference $S$ of the film at the time of measurement, or the exact linear equivalent of 90° of glancing angle.

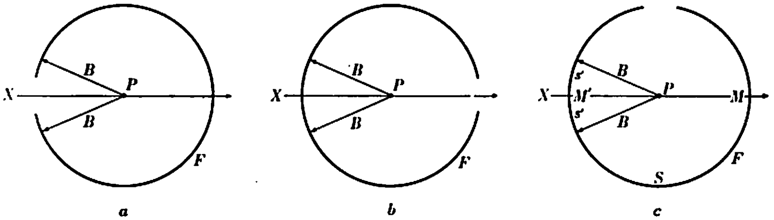


FIG. 1.—Three ways of loading an $x$-ray powder camera: ($a$) $x$-rays enter between the ends of the film; ($b$) $x$-rays leave between the ends of the film; ($c$) the points of entry and exit lie on an unbroken length of film giving an exact measure of the effective camera radius. $P$—powder sample. $F$—film. $X$—$x$-ray beam. $BB$—high-$\theta$ (back reflection) cone of diffraction. $M$—midpoint of low-$\theta$ rings. $M'$—midpoint of high-$\theta$ rings. $S$—semi-circumference of camera. $s's'$—semi-diameter of powder ring.

For the purpose of calibration an $x$-ray powder photograph was taken in this way, using a short, accurately centred, rotating copper wire 0.25 mm. in diameter, with Fe-$K\alpha\beta$ radiation. The film (Fig. 2) shows the U-shaped hole through which the beam entered the camera and the round hole through which the undiffracted beam emerged, with sharp diffraction rings centring at the corresponding positions $M'$ (90°$\theta$) and $M$ (0°$\theta$).

After drying for several weeks the film was measured on a travelling microscope reading to 0.001 mm. Repeated measurements agreed to ±0.01 mm. giving a degree of accuracy about ten times better than that obtained by an ordinary scale and hand-lens. To fix the positions $M$ and $M'$ all the lines were measured; the calibration measurements were confined to the high-$\theta$ rings, $(113)\alpha_1$, $(113)\alpha_2$, $(222)\alpha_1$, $(222)\alpha_2$, $(004)\beta_1$. The $\alpha$-doublets of (113) and (222) were clearly resolved on the film although the separation is barely visible in the reproduction.

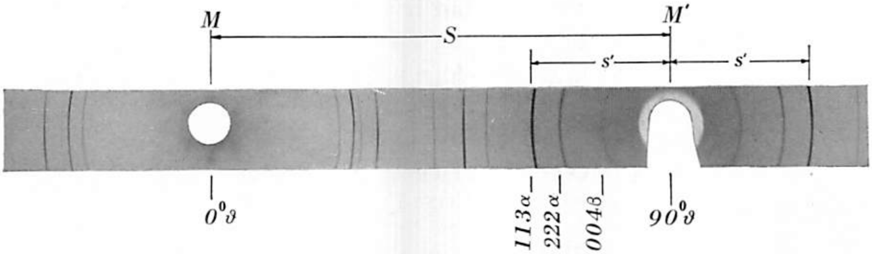


Fig. 2.—Calibration $x$-ray powder photograph of copper wire, with Fe-$K\alpha\beta$ radiation; symbols as in Fig. 1c.

From Figs. 1c and 2 it is clear that, having found $S$ from positions of $M$ and $M'$, and $2s$ for a diffraction ring $(hkl)$, the measured glancing angle is given, without regard to the nominal camera radius, by the expression:

$$\theta_{hkl}=90(1-s'/S)^\circ$$

Table 1 gives the measured glancing angles obtained in this way, and the corresponding calculated angles, from the formula:

$$\sin\theta_{hkl}=\tfrac{1}{2}\lambda\sqrt{h^2+k^2+l^2}/a_0$$

using the wave-lengths:[1]

$$\text{Fe-}K\alpha_2=1.93632\ \text{Å}$$
$$\text{Fe-}K\alpha_1=1.93239\ \text{Å}$$
$$\text{Fe-}K\beta_1=1.75329\ \text{Å}$$

and the cube-edge of copper:[2]

$$a_0=3.6079\ \text{Å}$$

---

[1] Siegbahn's values in X.U. (*International Tables for the Determination of Crystal Structures*, vol. 2, p. 586, 1935), converted to Å.

[2] From closely concordant precision measurements in *Strukturbericht*, vol. 3, p. 188, 1937.

The differences between the measured and calculated glancing angles are small and, except in the case of (222)$\alpha_1$, they decrease in a roughly linear manner with increasing $\theta$. The correction applied to this film, and others made under like conditions, was therefore taken from a straight line through the values given by (113)$\alpha_1$ and (004)$\beta_1$ Table 1 shows the effect of the linear correction on the recalculated cube-edge $a_0$. The rings (113)$\alpha_1$ and (004)$\beta_1$ of course give the original cube-edge; (113)$\alpha_2$ and (222)$\alpha_2$ give values which differ by only 0.0001 Å from the original length; (222)$\alpha_1$ is farther out of line, but it will be noted that the angular error is but 0.021° or 0.02 mm. on the film. The method thus reproduces the standard cube-edge with a high degree of precision.

TABLE 1

CALIBRATION MEASUREMENTS ON COPPER
($a_0$=3.6079 Å) USING FE-*K* RADIATION

| *hkl* | (113)$\alpha_1$ | (113)$\alpha_2$ | (222)$\alpha_1$ | (222)$\alpha_2$ | (004)$\beta_1$ |
|---|---|---|---|---|---|
| $\theta$ (measured) | 62.82 ° | 63.04 ° | 68.26 ° | 68.53 ° | 76.53 ° |
| $\theta$ (calculated) | 62.650 | 62.875 | 68.081 | 68.371 | 76.390 |
| Difference | 0.170 | 0.165 | 0.179 | 0.159 | 0.140 |
| Linear correction | −0.170 | −0.169 | −0.158 | −0.157 | −0.140 |
| $\theta$ (corrected) | 62.650 | 62.871 | 68.102 | 68.373 | 76.390 |
| $a_0$ | 3.6079 | 3.6080 | 3.6073 | 3.6078 | 3.6079 Å |

## COMMON PYRITE

Measurements of the cube-edge were made in the above described manner on samples from the following materials:

Pyrite, Leadville, Colorado (No. 26 in Smith, 1940; film No. 445). Large crystal with brass-yellow colour, flat-conchoidal fracture, and splendent lustre. Composition $FeS_{2.00 \pm 0.01}$ from independent analyses by Smith and Rogers. Qualitative test revealed no Ni (Smith) and no As (Rogers). Specific gravity 5.005±0.005 from 10 measurements on fragments from various parts of the crystal. Specific resistance at 20°, 32.6 ohms/cm. cube. Temperature coefficient of resistance, 20° to 200°, negative.

Pyrite, Rio Marina, Elba (No. 27 in Smith, 1940; film No. 449). Crystal with pale brass-yellow colour and small-conchoidal or rough fracture. Composition $FeS_{1.98 \pm 0.01}$ with trace of $SiO_2$, from two analyses (Smith). As, none

(Rogers). Au, none; Mn less than 0.0001 per cent; no other metal present in excess of 0.0001 per cent (Beamish). Specific gravity 5.020±0.005, from 10 measurements on fragments from various parts of the crystal. Specific resistance at 20°, 0.014 ohms/cm. cube. Temperature coefficient of resistance, 20° to 200°, positive.

The specific gravity measurements were made by the junior author using the torsion micro-balance described by Berman (1939). In view of the accuracy that was required numerous preliminary observations were made in an endeavour to reach an absolute accuracy of 0.1 per cent in the specific gravity measured on fragments weighing about 20 mg. Rather than assuming that the toluene used (Merck, B.P. 110-111°) had the density-temperature characteristics given for pure toluene in the *International Critical Tables*, a pure white cut diamond was used as a standard, assuming that its specific gravity was 3.511, as given by Williams (1932, p. 467) for "purest blue-white" diamond, in exact agreement with the calculated specific gravity. The effective density-temperature data for the toluene were thus obtained and used to determine the specific gravity of the pyrite samples. The specific gravity of the diamond was then determined in specially prepared carbon tetrachloride (B.P. 76.3°C, at 752 mm.), using the standard density-temperature data. The value obtained was 3.511, confirming the assumed specific gravity on which the pyrite values were based.

To avoid errors introduced by the noticeable hysteresis of the balance spring the balance was allowed to stand at 20 mg. for twenty minutes before making the weighings. The null point was then read after the balance had stood at zero for another twenty minutes. The null point obtained in this way was found to vary with temperature, and in practice it was found convenient to prepare a curve of null point and temperature and thus dispense with null point readings for each determination. Finally, it was found that weighings were reproducible to 0.003 mg. by estimating to one place beyond the vernier divisions of 0.01 mg.

The powder samples were in the form of minute spindles obtained by rolling the powder in collodion. Sharp films were obtained with Fe-$K\alpha\beta$ radiation. One of these films is reproduced in Fig. 3a, with indices against the rings that were used for the cell-edge determination. The other film shown, Fig. 3b, is that given by the nickeliferous pyrite which will be considered later.

TABLE 2

CUBE-EDGE OF COMMON PYRITE

| (*hkl*) | No. 26; $FeS_{2.00}$ | No. 27; $FeS_{1.98}$ |
|---|---|---|
| $(115)\alpha_1$ | 5.4075 | 5.4057 |
| $(115)\alpha_2$ | 5.4079 | (5.4054)* |
| $(025)\alpha_1$ | 5.4079 | 5.4063 |
| $(025)\alpha_2$ | 5.4080 | 5.4062 |
| $(125)\alpha_1$ | 5.4077 | 5.4067 |
| $(125)\alpha_2$ | 5.4082 | 5.4065 |
| Cube-edge: | 5.4079±0.0005Å | 5.4063±0.0005Å |

*Omitted from the average.

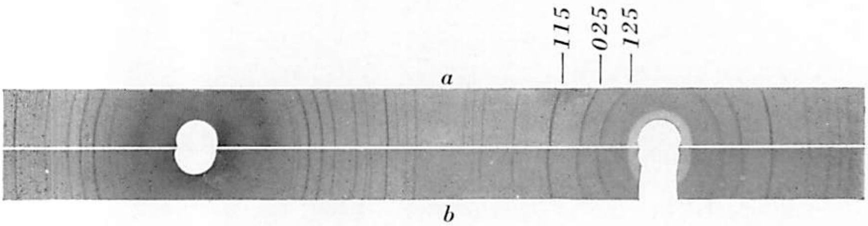


FIG. 3.—*X*-ray powder photographs of common pyrite, Leadville, Colorado (*a*), and nickeliferous pyrite, Sudbury, Ontario (*b*), with Fe-$K\alpha\beta$ radiation.

Table 2 gives the values of the cube-edge given by each ring measured on each film. From the consistency of the measurements it is clear that the two samples definitely differ in cell-edge. The new values lie in the range of the more exact values in the literature:

| | | |
|---|---|---|
| (Colorado) | 5.404±0.003 Å | de Jong (1927) |
| (Kongsberg) | 5.414±0.003 Å | Oftedal (1928) |
| | 5.405 Å | Parker and Whitehouse (1932) |

Both physically and chemically crystal No. 26 closely approaches perfection and therefore we would expect the calculated specific gravity of this crystal to agree well with the measured value. Using $1.649 \times 10^{-24}$ gm. as the mass associated with an atom of hydrogen, together with the ideal composition and the measured cube-edge, we obtain:

Specific gravity 5.003 (calculated)
5.005 (measured)

The good agreement accords with the apparent perfection of the crystal and suggests that the data obtained from this crystal closely represent the perfect pyrite crystal which appears to be relatively rare in nature.

The defect in sulphur, or the excess of iron, in crystal No. 27 might be due to one of three structural conditions: (*a*) interstitial iron atoms in a perfect pyrite structure; (*b*) vacant sulphur positions, giving 4(2.98) atoms per unit cell; (*c*) sufficient iron atoms in sulphur positions to give the composition $FeS_{1.98}$ in a structure having the full 4×3 atoms per unit cell. The first of these conditions may be dismissed as highly improbable in a structure of the pyrite type; the choice between the remaining alternatives may be decided by comparing the specific gravities calculated on each assumption with the measured value:

Specific gravity 4.981 (calc. for vacant S-positions)
5.014 (calc. for Fe in S-positions)
5.020 (measured)

Thus the assumption of structural imperfection due to iron atoms in sulphur positions is admitted whereas the possibility of vacant sulphur positions is excluded. The accepted type of structural imperfection is the same as that found in much greater degree in skutterudite-smaltite, $CoAs_{3-x}$, in which some cobalt atoms occupy arsenic positions (Peacock and Berry, 1940, p. 65). On the other hand, the usual excess of sulphur in pyrrhotite, $FeS_{1+x}$, has been attributed to the alternative type of structural imperfection, namely vacant iron positions (Hägg and Sucksdorff, 1933).

Without entering a discussion of the bearing of these results on the problem of the variable conductivity of pyrite[3] it is of interest to note that the apparently perfect pyrite crystal, with its high resistance and negative temperature coefficient, has typically semimetallic character, whereas the imperfect crystal with iron in sulphur positions, low resistance, and positive temperature coefficient, is more metallic in its behaviour.

---

[3] A full account of the completed work on this problem, by the second author, is being prepared for publication elsewhere.

## NICKELIFEROUS PYRITE

Nickeliferous pyrite with 6½ per cent Ni, or about half an atom of Ni per unit cell, was recently described from Sudbury, Ontario, by Thomson and Allen (1939). The hand specimen has the colour of pyrite modified by a faint violet shade, which is also apparent in polished sections. Variation in the distribution of the faint violet colour was thought to be related to variation in nickel-content. From information supplied by Peacock it was stated that the cube-edge of the nickeliferous pyrite does not differ appreciably from that of common pyrite.

More recently Bannister (1940) has shown that two specimens of bravoite $(Fe,Ni)S_2$, with 1.41 and 2.42 atoms of nickel per unit cell, respectively, have the structure of pyrite and that the cube-edges show a regular increase from that of pyrite to that of artificial $NiS_2$. The expected cube-edge of nickeliferous pyrite with half an atom per unit cell is thus 5.42 Å, which is slightly greater than 5.405Å (Parker and Whitehouse, 1932). Bannister suggested, therefore, that this difference was overlooked, or that there is a discontinuity in the series of mixed crystals $FeS_2$—$(Fe,Ni)S_2$.

Since the original powder films were not suitable for very exact measurements, having been made with Cu-radiation which gives a dark background with iron minerals, especially in the sensitive high-$\theta$ region, a photograph was taken from a typical sample of the nickeliferous pyrite supplied by Professor Thomson, using the new back-reflection method with Fe-radiation. The film (Fig. 3b) is fairly clear, but the $\alpha$-doublets are not resolved, suggesting some inhomogeneity, as inferred by Thomson. Furthermore, a few faint extra lines are visible; these do not correspond with the strongest lines of millerite, NiS, or of pentlandite, (Fe,Ni)S, or of violarite, $(Ni,Fe)_3S_4$ (Bannister, 1941), and the nature of the small amount of impurity from which they were derived was not determined.

Three sets of measurements on the film of nickeliferous pyrite are given below:

| (*hkl*)........ | (115) | (025) | (125) |
|---|---|---|---|
| $a_0$.......... | 5.418 Å | 5.418 Å | 5.420 Å |
| | 5.417 | 5.420 | 5.421 |
| | 5.418 | 5.420 | 5.421 |

The mean value, $a_0 = 5.419 \pm 0.002$ Å, is indeed appreciably higher than the cube-edge of common pyrite and exactly equal to the value predicted by Bannister.

Fig. 4 shows the variation of cube-edge with nickel-content

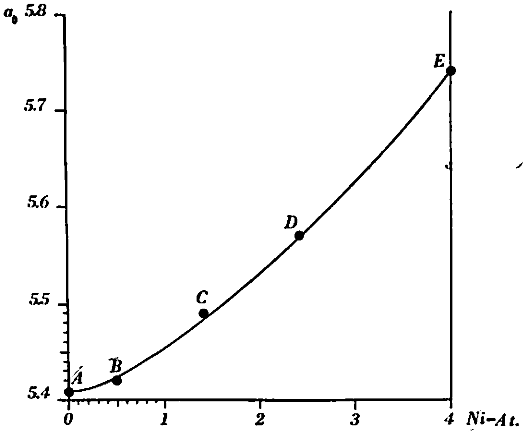


FIG. 4.—Relation of cube-edge to nickel-content in crystals with the composition $(Fe,Ni)S_2$ and the structure of pyrite; *A*—pyrite, Colorado; *B*—nickeliferous pyrite, Sudbury; *C*—bravoite, Derbyshire; *D*—bravoite, Rhenish Prussia; *E*—Artificial $NiS_2$.

(Ni-atoms per unit cell) in crystals with the composition $(Fe,Ni)S_2$ and the pyrite type of structure, using the following data:

| | *A* | *B* | *C* | *D* | *E* | |
|---|---|---|---|---|---|---|
| Nickel-content....... | 0 | 0.55 | 1.41 | 2.42* | 4 | atoms/cell |
| Cube-edge........... | 5.408 | 5.419 | 5.49 | 5.57 | 5.74 | Å |

*A*—Pyrite, Leadville, Colorado (this paper). *B*—Nickeliferous pyrite, Denison Mine, Sudbury district, Ontario (Thomson and Allen, 1939, and this paper). *C*—Bravoite, Mill Close Mine, Derbyshire (Bannister, 1940). *D*—Bravoite, Mechernich, Rhenish Prussia (Bannister, 1940). *E*—Artificial $NiS_2$ (de Jong and Willems, 1927). *Includes cobalt.

The points lie nearly on a curve which may therefore be used to obtain the approximate nickel-content of a nickel-pyrite from the easily measured cell-edge. But in drawing this curve it is not implied that the entire series is known or likely to be found in nature. Bannister (1941) has emphasized the absence of natural bravoites in the region between *D* and *E* and has shown that violarite from the Vermilion Mine, Sudbury district, is not a nickel-pyrite but an iron-polydymite with the composition $(Ni,Fe)_3S_4$ and the spinel-type of structure.

The fact that nickeliferous pyrites between *A* and *B* are known (Thomson and Allen, 1939) indicates continuity of the series in this region. However, the curve will probably not give an accurate measure of the nickel-content in this range owing to the possible interference of sulphur deficiency which, as we have shown, reduces the cube-edge in pyrite and may therefore counteract the increase due to small proportions of nickel in place of iron.

## SUMMARY

Using a precise method for measuring the cube-edge, and certain precautions in determining specific gravity with Berman's balance, the following data were obtained. Pyrite, Leadville, Colorado; $FeS_{2.00\pm0.01}$, free from Ni and As:$a_0 = 5.4079\pm0.0005$ Å; G = 5.005±0.005 (meas.), 5.003 (calc.). Pyrite, Rio Marina, Elba; $FeS_{1.98\pm0.01}$, $SiO_2$ trace, As none, Au none, Mn <0.0001 per cent: $a_0 = 5.4063\pm0.0005$ Å; G = 5.020 (meas.), 5.014 (calc. for Fe-atoms in S-positions), 4.981 (calc. for vacant S-positions). Nickeliferous pyrite, Denison Mine, Sudbury district, Ontario; Ni 6.50 per cent: $a_0 = 5.419\pm0.002$ Å. Deficiency of sulphur in pyrite is accompanied by iron atoms in sulphur positions. There appears to be no discontinuity in pyrite mixed crystals with 0 to $\frac{1}{2}$ atoms of nickel per unit cell.

## REFERENCES

BANNISTER, F. A. (1940): Bravoite from Mill Close Mine, Derbyshire—*Min. Mag.*, vol. 25, pp. 609-614.

———— (1941): The crystal structure of violarite—*Min. Mag.*, vol. 26, pp. 16-18.

BERMAN, H. (1939): A torsion microbalance for the determination of specific gravities of minerals—*Am. Mineral.*, vol. 24, pp. 434-440.

BUERGER, M. J. (1936): An *x*-ray powder camera—*Am. Mineral.*, vol. 21, pp. 11-17.

HÄGG, GUNNAR, and SUCKSDORFF, INGRID (1933): Die Kristallstruktur von Troilit und Magnetkies—*Zeits. physikal. Chem.*, B, vol. 22, pp. 444-452.

JONG, W. F. de (1927): Een methode van belichting van kristalpoeder met röntgenstralen—*Physica*, vol. 7, pp. 23-28.

———— and WILLEMS, H. W. V. (1927): Existenz und Struktur der Disulfide $NiS_2$ and $CoS_2$—*Zeits. anorg. Chem.*, vol. 160, pp. 185-189.

OFTEDAL, IVAR (1928): Über die Kristallstrukturen der Verbindungen $RuS_2$, $OsS_2$, $MnTe_2$ und $AuSb_2$. Mit einem Anhang über die Gitterkonstante von Pyrit—*Zeits. physikal. Chem.*, vol. 135, pp. 291-299.

PARKER, H. M. and WHITEHOUSE, W. J. (1932): An $x$-ray analysis of iron pyrites by the method of Fourier Series—*Phil. Mag.*, vol. 14, pp. 939-961.

PEACOCK, M. A. and BERRY, L. J. (1940): Röntgenographic observations on ore minerals—*Univ. Toronto Studies, Geol. Ser.*, no. 44, pp. 47-69.

SMITH, F. GORDON (1940): Variation in the electrical conductivity of pyrite—*Univ. Toronto Studies, Geol. Ser.*, no. 44, pp. 83-93.

THOMSON, ELLIS, and ALLEN, J. S. (1939): Nickeliferous pyrite from the Denison Mine, Sudbury district, Ontario—*Univ. Toronto Studies, Geol. Ser.*, no. 42, pp. 135-138.

WILLIAMS, ALPHEUS F. (1932): *The genesis of the diamond*, vol. 2—London.

# PILLOW LAVAS FROM THE DRYDEN-WABIGOON AREA KENORA DISTRICT, ONTARIO[1]

By J. SATTERLY
*Ontario Department of Mines*

The purpose of this paper is to present some new analyses of pillow lavas, and draw comparisons with other published analyses of Keewatin pillow lavas, noting the paucity of analytical information concerning them. Specific gravity determinations of a number of the lavas are given with a discussion of their usefulness in distinguishing the different lava species.

During the 1939 and 1940 field seasons the writer was in charge of a field party of the Ontario Department of Mines in the Dryden-Wabigoon area, Kenora district (Fig. 1). The town of Dryden, on the main line of the Canadian Pacific Railway, is approximately halfway between Winnipeg and Fort William. The general geology has been briefly reviewed in a preliminary report on the field work in 1939, part of which was reproduced in a later paper (1940, pp. 75-6).

The best exposures of the lavas are to be found on the lake shores, and in a burnt area in the south half of Brownridge Township. The level of Wabigoon Lake has been raised by a dam at Dryden with the result that storm waves have removed in many localities the clay capping from the glaciated outcrops exposing excellent sections through the vertical pillow lavas. The low water levels prevailing during the two field seasons made available for study many outcrops usually covered.

Owing to the fine grain and alteration of the lavas, the original mineral composition and rock type cannot often be determined with any degree of precision by microscopic examination. An effort was made to use specific gravity as a means of differentiation and, to test this possibility, the following data are submitted.

---

[1] Published with the permission of the Provincial Geologist of the Ontario Department of Mines.

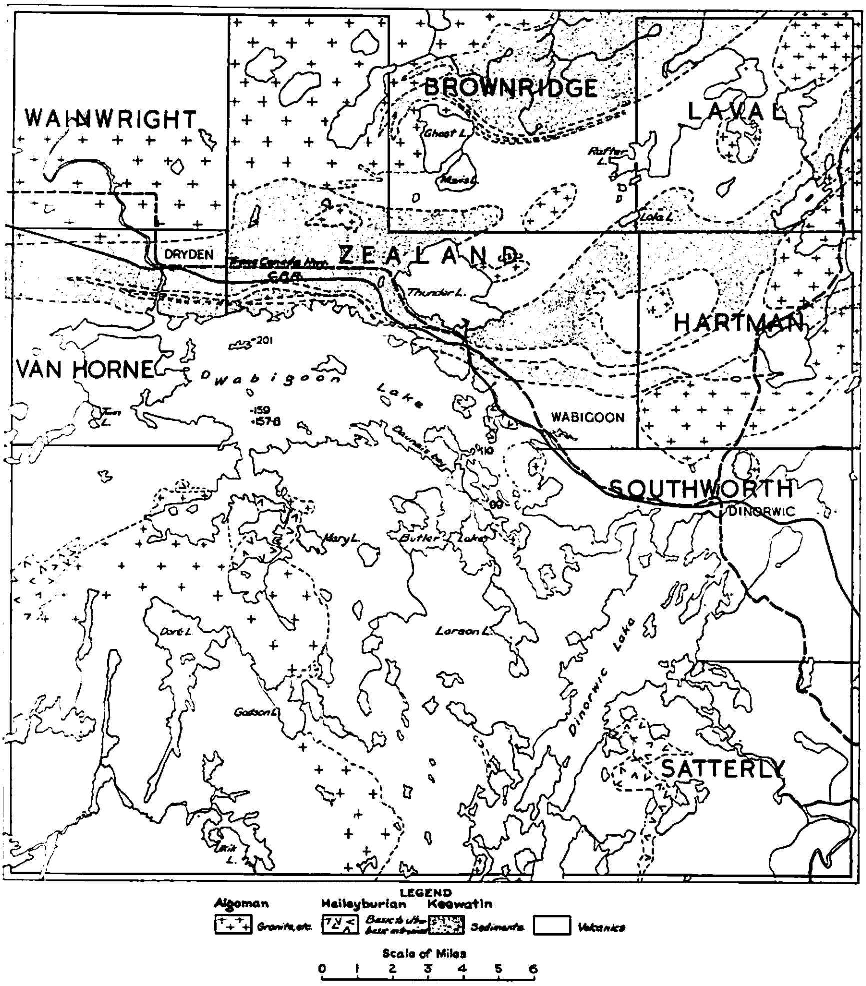


FIG. 1.—Geological map of the Dryden-Wabigoon area, Kenora district, Ontario.

TABLE 1

SPECIFIC GRAVITIES OF LAVAS FROM THE DRYDEN-WABIGOON AREA

| Rock | Locality | Sp.Gr. |
|---|---|---|
| 1. Dark green pillow lava | Island No. 201, Wabigoon Lake. | 3.112* |
| 2. Greenish-black pillow lava | Rafter Lake, Brownridge Township | 3.03 |
| 3. Porphyritic pillow lava (analysed) | East of Mavis Lake, Brownridge Township | 3.021* |
| 4. Amygdaloidal pillow lava | East of Ghost Lake, Brownridge Township | 2.97 |
| 5. Greenish-gray lava | Butler Lake | 2.91 |
| 6. Pale gray pillow lava | Lot 1, Con. 1, Southworth Township | 2.88 |
| 7. Greenish-gray porphyritic lava | Butler Lake | 2.872* |
| 8. Amygdaloidal lava | Rafter Lake, Brownridge Township | 2.87 |
| 9. Gray pillow lava (analysed) | Islands No. 157-8, Wabigoon Lake | 2.870* |
| 10. Greenish-gray flinty lava | Mary Lake | 2.844 |
| 11. Black, flinty lava | Mary Lake | 2.774 |
| 12. Greenish-gray amygdaloidal lava | Larson Lake | 2.72 |
| 13. Dove-gray lava | Daunais Bay, Wabigoon Lake | 2.70 |
| 14. Black flinty lava (analysed) | Near Lola Swamp, Laval Township | 2.65 |

*Specific gravity determinations by the Provincial Assay Office; others by the writer with apparatus lent by the Department of Physics, University of Toronto.

Before discussing the above results the average specific gravities for some volcanic rocks are given in Table 2 for comparison.

TABLE 2

AVERAGE SPECIFIC GRAVITIES OF VOLCANIC ROCKS

| Rock | Average Sp. Gr. | |
|---|---|---|
| 1. Island basalt (Atlantic) | 2.954 | (Daly, 1933, p. 47) |
| 2. Plateau basalt | 2.930 | (Daly, 1933, p. 47, av. of averages) |
| 3. Island basalt (Pacific and Indian) | 2.827 | (Daly, 1933, p. 47) |
| 4. Basalt | 2.87 | (Johannsen, 1937, III, p. 262) |
| 5. Andesite | 2.656* | (Washington, 1917) |
| 6. Dacite | 2.598* | (Washington, 1917) |
| 7. Rhyolite | 2.510* | (Washington, 1917) |

*Values for Nos. 5, 6, 7, computed by the writer from 149, 42, and 34, Sp. gr. values, respectively, given in Washington for rocks so named by the authors.

Referring to the rocks in Table 1, it was thought in the field from their appearance that Nos. 1, 2, 3, 4, 6, and 8 were basic, 5, 7, 9, and 12 intermediate, and 10, 11, 13, and 14 acid lavas. However, by comparison with the average specific gravities given in Table 2 it is apparent that practically all of the lavas tested from the Dryden-Wabigoon area have specific gravities higher than that given for andesite, namely 2.656, and that the majority of them are higher than the average for all basalts, namely 2.87. Therefore, on the basis of specific gravity determinations alone most of the lavas in the Dryden-Wabigoon area would be considered to be basaltic in composition. In view of the chemical data presented later it is suggested that despite the excellent preservation of pillow structures, and other volcanic textures, that the increased density is due to the development of a new mineral assemblage and a decrease in original pore space owing to compression and metamorphism. In fact, the values obtained appear to be more closely comparable with those given by Daly for plutonic igneous types, namely gabbro 2.976; diorite 2.781; tonalite 2.751; granite 2.667 (Daly, 1933, p. 47). It must be admitted, therefore, that for purposes of identification specific gravity determinations of early pre-Cambrian lavas appear to be of little value.

The pillow lavas show great diversity in colour, size, shape, and composition. Various shades of green are the most common, grading into black or pale gray as extremes. On island and shore outcrops on Wabigoon and Butler Lakes pillows are beautifully displayed (Fig. 2). Undeformed pillows range in size from a few inches to many feet. On Island No. 159, Wabigoon Lake, a pillow 6 by 25 feet in dimensions was seen, and on Island No. 110, Wabigoon Lake, a pillow showing six rows of vesicles at its top is 3-4 feet thick and has an exposed length of 20 feet (Fig. 3). It is from exposure material of this type that structural determinations were made, the position of the vesicles and the packing of the pillows indicating that the top of the lava flow is away from the observer. In contrast to such material the pillow lavas may be highly deformed, the selvages of the pillows being twisted and crumpled in such a manner as to suggest that the rock was in a quasi-solid condition during the period of deformation (Figs. 4, 7).

In some of the pillow lavas, concentric structures, similar to those in an onion, are very common. Minute white quartz stringers spaced one-half to one inch apart or even closer, occur parallel to the pillow selvages. Excellent exposures of this type may be seen at many places, but easily accessible exposures are Islands Nos. 157-8, Wabigoon Lake, where the pillows range up to 3-7 feet; and an outcrop between Butler and Wabigoon Lakes (south of Island No. 99) where 100 stringers of quartz were counted in a single pillow. On an outcrop one mile south of Twin Lakes, Van Horne Township, sixty quartz stringers were counted in a width of 13 inches. These stringers are presumably secondary and are thought to fill peripheral cracks formed as a result of cooling. Concentric structures in pillows have been noted by Lewis (1914, p. 650), Moore (1930), and Hurst (1932).

FIG. 2.—Pillow lava, Island No. 110, Wabigoon Lake, Kenora district, Ontario. Striations are glacial striae. Note peripheral zone of vesicles.

An analysis by the Provincial Assay Office of concentric, gray pillow lava from Islands No. 157-8, Wabigoon Lake, is given in

Table 3. The specimen was taken from the centre of a pillow and appeared to be free of the minute quartz stringers noted above. Two other analyses are included for comparison.

It will be noticed from the data given in Table 3 that the composition of the pillowed andesite from Wabigoon Lake is very similar to that of the Japanese andesite quoted. Comparisons with average analyses of andesite, quartz basalt, and basalt (Daly, 1933, pp. 16, 17, 18) show that the Wabigoon rock is nearest to the quartz basalt in composition.

FIG. 3.—Glaciated outcrop of pillow lava, Island No. 110, Wabigoon Lake, Kenora district, Ontario. Pillow with hammer on it is 3 to 4 feet thick and has an exposed length of 20 feet. The hammer is at the bottom of the pillow; note the six rows of vesicles at the top.

In Table 4 are given the norm and recast for this pillowed andesite. It will be seen that normative quartz amounts to 21.48 per cent. Microscopic examination shows that the rock has been intensely altered, one minute quartz stringer was seen in addition to scattered grains of quartz in the groundmass of the rock. Quartz has been introduced, but to what extent it is impossible to say. The rock consists of an aggregate of quartz grains, laths and relict phenocrysts of andesine, grains of epidote, minute shredded prisms of hornblende, lenticular aggregates of penninite with a little biotite, and accessory carbonate and rutile. From the tabulated and descriptive information the original rock is classified as a pillowed porphyritic andesite, or silicified basalt.

TABLE 3

PILLOWED ANDESITE AND RELATED ROCKS

| | 1 | 2 | 3 |
|---|---|---|---|
| $SiO_2$ | 58.59 | 59.47 | 55.46 |
| $Al_2O_3$ | 16.94 | 17.12 | 16.85 |
| $Fe_2O_3$ | 1.50 | 2.33 | 2.13 |
| FeO | 5.09 | 5.69 | 4.86 |
| MgO | 5.17 | 4.04 | 6.31 |
| CaO | 6.38 | 7.24 | 7.86 |
| $Na_2O$ | 1.88 | 2.23 | 3.30 |
| $K_2O$ | 0.39 | 0.30 | 1.40 |
| $H_2O$ | 2.14 | 1.35 | 0.58 |
| $TiO_2$ | 0.95 | .... | 0.88 |
| $P_2O_5$ | 0.21 | .... | 0.15 |
| MnO | 0.23 | .... | 0.22 |
| $Cr_2O_3$ | 0.03 | .... | .... |
| $FeS_2$ | 0.45 | .... | .... |
| $CO_2$ | 0.28 | .... | .... |
| | 100.23 | 99.77 | 100.00 |
| Symbol | II.4.4.(4)5 | II.4.4."5 | .... |

1. Pillowed andesite, Islands No. 157-8, Wabigoon Lake, Kenora district, Ontario. Sp. gr. 2.870.
2. Andesite, Bandai San, Japan (Washington, 1917, anal. No. 72, p. 416).
3. Quartz basalt, average of 14 analyses (Daly, 1933, p. 18).

In Brownridge Township, particularly between Mavis and Rafter Lakes, the country has been severely burnt and the rock ridges in many places are very clean, giving fine exposures of the lavas. The pillow lavas form bands from 10 to over 100 feet in thickness, but average 30 feet. Between these bands are bands of medium-grained material, now an amphibolite, representing the coarser part of the lava flows. These show a similar range in thickness and the average thickness of the flows in Brownridge Township is therefore approximately 60 feet. Sandberg (1938, pp. 814-15) has given data for Keweenawan basalt flows showing that they range from inches to more than 200 feet in thickness, with averages for three types between 30 and 90 feet. In Scotland, Ireland, and the Faroes Tertiary basalt flows show a range from 6 to 70 feet, with an average of about 45 feet (Geikie, 1897, vol. 2, p. 192). These figures show that the Keewatin lava flows in the Dryden-Wabigoon area have thicknesses very similar to those of younger flows.

TABLE 4

NORM AND RECAST OF PILLOWED ANDESITE, WABIGOON LAKE

| Norm | | Recast | |
|---|---|---|---|
| Quartz | 21.36 | Quartz | 32.70 |
| Orthoclase | 2.22 | Andesine | 15.33 |
| Albite | 16.24 | Epidote | 11.49 |
| Anorthite | 31.69 | Hornblende | 22.73 |
| Corundum | 1.73 | Penninite | 11.22 |
| Hypersthene | 19.90 | Biotite | 3.77 |
| Ilmenite | 1.82 | Siderite | 0.67 |
| Magnetite | 2.09 | Rutile | 0.96 |
| Pyrite | 0.45 | Pyrite | 0.45 |
| Unassigned | 2.66 | Unassigned | 0.89 |
| | 100.16 | | 100.21 |

The bulk of the pillow lavas in Brownridge Township are believed to be basaltic in composition and have narrow dark green to black selvages. They may or may not be amygdaloidal. The amygdaloids are often peripheral, and in a few cases are confined to the top of the pillows, thus giving additional support to the determination of the attitude of these vertical flows from the shapes and packing of the pillows (Fig. 5).

In the lava assemblage in Brownridge Township a lava composed of well-developed phenocrysts of uralitized augite, up to one-tenth of an inch diameter set in a fine-grained dark green groundmass, was found at a number of localities. It is thought these occurrences represent one flow horizon. This flow frequently exhibits pillow structures, and although in most localities they are somewhat deformed, in an outcrop half-way between Mavis and Rafter Lake they are well preserved and exhibit a faint concentric structure (Fig. 6). Under the microscope in thin section the rock is found to consist of stumpy phenocrysts of hornblende (uralitized augite) in a groundmass composed of plagioclase, hornblende, quartz, biotite, epidote, carbonate, sphene, and ilmenite. The rock has been largely recrystallized.

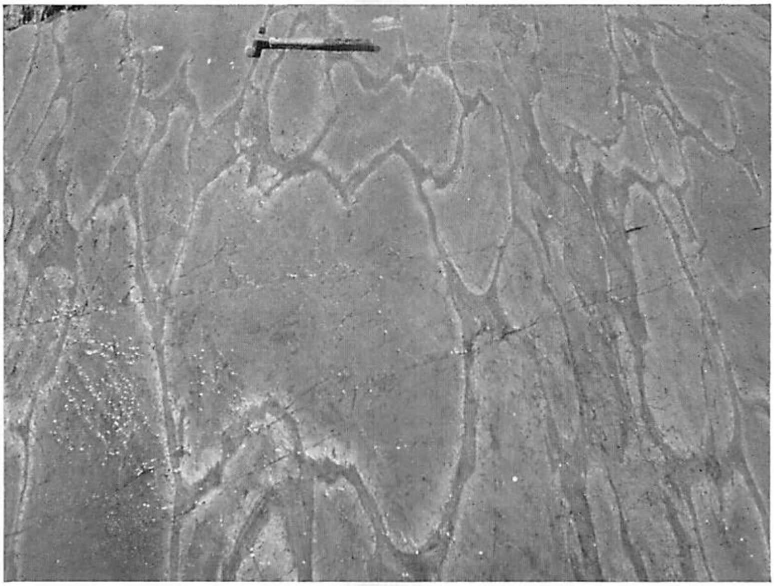


FIG. 4.—Highly deformed pillow lava. Reef off Anderson Island, Wabigoon Lake, Kenora district, Ontario.

An analysis by the Provincial Assay Office, with some others for comparison, is given in Table 5.

TABLE 5

ANALYSES OF PILLOWED AUGITE-BASALT AND RELATED ROCKS

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $SiO_2$.......... | 47.10 | 48.28 | 49.06 | 48.80 | 47.70 |
| $Al_2O_3$......... | 15.93 | 13.32 | 15.70 | 13.98 | 15.30 |
| $Fe_2O_3$......... | 3.43 | 1.70 | 5.38 | 3.59 | 5.93 |
| FeO.......... | 7.06 | 10.47 | 6.37 | 9.78 | 4.85 |
| MgO......... | 7.40 | 10.41 | 6.17 | 6.70 | 7.31 |
| CaO.......... | 12.04 | 11.93 | 8.95 | 9.38 | 11.83 |
| $Na_2O$......... | 2.98 | 0.78 | 3.11 | 2.59 | 2.46 |
| $K_2O$.......... | 0.44 | 0.88 | 1.52 | 0.69 | 0.61 |
| $H_2O$.......... | 1.09 | 1.52 | 1.62 | 1.80 | 0.44 |
| $TiO_2$.......... | 1.12 | 0.26 | 1.36 | 2.19 | 1.45 |
| $P_2O_5$.......... | 0.01 | 0.06 | 0.45 | 0.33 | 0.29 |
| MnO.......... | 0.39 | ..... | 0.31 | 0.17 | 0.46 |
| $Cr_2O_3$......... | Trace | ..... | ..... | ..... | ..... |
| $FeS_2$.......... | None | ..... | ..... | ..... | ..... |
| $CO_2$.......... | 1.21 | 0.59 | ..... | ..... | 1.87 |
| | 100.20 | 100.20 | 100.00 | 100.00 | 100.61 |
| Symbol.... | ''III.5.''4.3 | | | | |

1. Pillowed augite-basalt, Brownridge Township, Kenora district, Ontario. Sp. gr. 3.021.
2. Pillowed basalt, Sandborn Bay, Sandy Lake, Kenora district (Patricia Portion), Ontario (Satterly, 1938, p. 11). Sp. gr. 2.916.
3. Average of 198 analyses of basalts (Daly, 1933, p. 17).
4. Average of 43 analyses of Plateau basalts (Daly, 1933, p. 17).
5. Augite-basalt, Cedar Ranch Mesa, Arizona (Robinson, 1913, p. 150); incl. SrO 0.02, BaO 0.09, Cl trace, $SO_3$ none.

The analyses given for comparison show that the pillow lava has a higher lime content than the average basalt, and a potash content close to that of the average Plateau basalt, while the Arizona augite-basalt is practically identical in composition.

Pillowed acid lavas are not common in the area, but in Brownridge Township at several horizons acid lava forms bands that mapping showed to be continuous. These bands range from 50 to 150 feet in thickness. The rocks are highly deformed, but in a few cases show fair pillow structures (Fig. 7). Amygdaloidal structure is not unusual and is preserved despite the metamorphism. Red garnets are not uncommon and but for the volcanic structures mentioned the rocks in places have lithological characters similar to siliceous sediments. A thin section of a pillowed amygdaloidal acid lava from one mile east of Mavis Lake shows that it has been completely recrystallized. The groundmass consists of an aggregate of feldspar, quartz, biotite, white mica, and grains of iron ores. The amygdaloids exhibit a zoning, the centre zone being a coarse aggregate of quartz with some biotite flakes, and the marginal zone a fine-grained aggregate of quartz with feldspar (?) and black dust (magnetite?).

FIG. 5.—Pillow lava, south-east of Mavis Lake, Brownridge Township, Kenora district, Ontario. Note that the vesicles and amygdales are confined to the tops of the pillows. The marks on the hammer handle are an inch apart.

A somewhat similar amygdaloidal, flinty, black, acid lava was found in Laval Township, one mile north-east of Lola Lake. Owing to its cryptocrystalline texture microscopic determination of all the minerals is impossible. The rock is completely recrystallized.

The amygdaloids are ovoid structures with a rim composed of an aggregate of brown biotite flakes, some feldspar(?), and rarely grains of magnetite, and an occasional crystal of hornblende. The interior of the amygdaloid is an aggregate of colourless minerals with minute black dust and disseminated flakes of biotite. The groundmass consists of an aggregate of colourless minerals and flakes of biotite. An analysis of this rock by the Provincial Assay Office is given in Table 7.

FIG. 6.—Pillowed augite andesite, east of Mavis Lake, Brownridge Township, Kenora district, Ontario. Note the faint concentric structures in the pillows, and the inclusions of sediments in the pillow interspaces. The black mineral is uralitized augite.

These analyses would suggest that the acid lava is an altered dacite. It is therefore probable that the pillowed lavas are not more acid than dacite. Wilson (1938, p. 77) states that in the Noranda district in Quebec pillow structure is present in local dacitic phases of rhyolite, but not in the normal rhyolite.

Although it has been admitted that "it is perhaps debatable

## TABLE 6

### NORM AND RECAST OF PILLOWED AUGITE-BASALT

| Norm | | Recast | |
|---|---|---|---|
| Orthoclase | 2.22 | Hornblende | 47.09 |
| Albite | 25.15 | Labradorite, An 58 | 27.38 |
| Anorthite | 28.91 | Quartz | 9.96 |
| Diopside | 18.88 | Epidote | 5.21 |
| Hypersthene | 2.62 | Biotite | 3.72 |
| Olivine | 11.50 | Calcite | 2.70 |
| Ilmenite | 2.13 | Ilmenite | 1.06 |
| Magnetite | 4.87 | Sphene | 1.36 |
| Calcite | 2.70 | Unassigned | 2.24 |
| Unassigned | 1.10 | | |
| | 100.08 | | 100.72 |

## TABLE 7

### ANALYSES OF DACITES

| | 1 | 2 | 3 |
|---|---|---|---|
| $SiO_2$ | 68.45 | 65.68 | 62.90 |
| $Al_2O_3$ | 14.82 | 16.25 | 18.29 |
| $Fe_2O_3$ | 1.11 | 2.38 | 1.79 |
| FeO | 4.75 | 1.90 | 4.00 |
| MgO | 1.58 | 1.41 | 1.61 |
| CaO | 2.34 | 3.46 | 5.62 |
| $Na_2O$ | 2.60 | 3.97 | 2.91 |
| $K_2O$ | 1.94 | 2.67 | 1.48 |
| $H_2O$ | 0.55 | 1.50 | 0.90 |
| $TiO_2$ | 0.97 | 0.57 | 0.18 |
| $P_2O_5$ | None | 0.15 | .... |
| MnO | 0.08 | 0.06 | .... |
| $Cr_2O_3$ | None | .... | .... |
| $FeS_2$ | 0.22 | .... | .... |
| $CO_2$ | 0.38 | .... | .... |
| | 99.79 | 100.00 | 99.68 |

1. Acid lava, Laval Township, Kenora district, Ontario. Sp. gr. 2.65.
2. Average of 90 analyses of dacites (Daly, 1933, p. 15).
3. Dacite, Kosona, Methana, Greece (Johannsen, 1932, p. 395). Sp. gr. 2.464.

whether the present composition of the metamorphosed Keewatin basalts is sufficiently like the original composition to be of much value for purposes of comparison" (Cooke, James, and Mawdsley, 1931, p. 29) it has been shown by them that the analyses are comparable. The writer lists in Tables 8 and 9 all the analyses of Keewatin basalts and pillow lavas respectively that he has been able to find in the reports of the Ontario Department of Mines, Quebec Bureau of Mines, Geological Survey of Canada, and a limited examination of the geological literature. In each table the average has been given, and also in Table 9 that for the average Plateau basalt. It will be noted that except for the alumina, water, and carbon dioxide there is an excellent correspondence between the calculated averages and that of the Plateau basalt.

FIG. 7.—Deformed pillowed acid lava, east of Mavis Lake, Brownridge Township, Kenora district, Ontario. Pillows show a wavy concentric structure and amygdales.

The writer is of the opinion that the many green lavas so often mapped as andesites are actually basalts and that they are green

## TABLE 8

### ANALYSES OF KEEWATIN BASALTS AND ANDESITES

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 45.44 | 45.67 | 46.34 | 46.66 | 48.10 | 48.64 | 49.30 | 50.65 | 52.89 | 54.02 | 54.44 | 48.19 |
| $Al_2O_3$ | 20.33 | 19.94 | 19.31 | 15.47 | 17.14 | 14.81 | 14.63 | 14.57 | 17.23 | 15.67 | 17.63 | 17.05 |
| $Fe_2O_3$ | 3.07 | 1.44 | 5.80 | 3.16 | 6.68 | 6.02 | 2.63 | 2.31 | 1.39 | 2.38 | 7.18 | 4.06 |
| FeO | 5.40 | 10.04 | 10.14 | 8.48 | 11.83 | 9.78 | 9.10 | 11.59 | 7.22 | 8.46 | 6.12 | 9.29 |
| MgO | 4.76 | 0.41 | 1.13 | 3.99 | 4.33 | 4.56 | 6.51 | 4.34 | 2.71 | 4.12 | 3.19 | 3.64 |
| CaO | 12.12 | 8.30 | 10.22 | 9.69 | 7.09 | 7.28 | 11.00 | 6.70 | 8.51 | 7.14 | 2.83 | 8.99 |
| $Na_2O$ | 2.33 | 2.65 | 2.07 | 2.06 | 2.68 | 1.72 | 0.19 | 2.45 | 4.13 | 4.84 | 4.03 | 2.25 |
| $K_2O$ | 0.45 | 0.24 | 1.00 | 0.35 | 0.48 | 4.10 | 0.30 | 0.59 | 0.34 | 0.64 | 1.49 | 0.87 |
| $H_2O$ | 3.23 | 4.66 | 2.08 | 4.27 | 2.00 | 2.18 | 3.07 | 2.67 | 0.87 | 0.81 | 2.04 | 2.78 |
| $TiO_2$ | 0.52 | .... | .... | .... | .... | .... | 0.83 | 1.31 | 2.91 | 1.63 | .... | .... |
| $P_2O_5$ | 0.04 | .... | .... | .... | .... | .... | 0.14 | 0.11 | 0.33 | 0.44 | .... | .... |
| $CO_2$ | 2.20 | 6.77 | .... | 6.11 | .... | 0.88 | 2.10 | 2.40 | 1.41 | nil | 1.64 | 2.43 |
| MnO | .... | .... | .... | .... | .... | .... | .... | 0.32 | 0.20 | 0.01 | .... | .... |
| $FeS_2$ | .... | .... | .... | .... | .... | .... | 0.34 | 0.28 | 0.23 | .... | .... | .... |
| | 99.89 | 100.12 | 98.09 | 100.24 | 100.33 | 99.97 | 100.14 | 100.29 | 100.37 | 100.18 | 100.59 | 99.55 |

1. Altered basalt, Fly Lake, Kenora district, Ontario (Bateman, 1939, p. 14). S trace.
2. "Basalt," Porcupine Area, Ontario (Burrows, 1925, p. 20).
3. Basalt, Tudor Township, Hastings County, Ontario (Miller and Knight, 1914, p. 84).
4. "Basalt", Porcupine Area, Ontario (Burrows, 1925, p. 20).
5. Basalt, Tudor Township, Hastings County, Ontario (Miller and Knight, 1914, p. 84).
6. Bluish black slag-like material in surface of lava, Cook Township, Cochrane district (Wright, 1922, p. 39).
7. Basalt, Benton Township, Sudbury district (Laird, 1935, p. 10). Sp. gr. 3 031.
8. Freshest greenstone, Uchi Mine, Kenora district (Bateman, 1939, p. 32). Sp. gr. 2 82.
9. Basalt, Shoal Lake, Kenora district (Thomson, 1936, p. 46). Sp. gr. 3.022
10. Massive andesite, Dufresnoy Township, Abitibi County, P.Q. (Wilson, 1938, p. 79). S 0.09.
11. Andesite, Madoc Area, Ontario (Miller and Knight, 1914, p. 64).
12. Average of 1-9, basalts.

## TABLE 9

### ANALYSES OF KEEWATIN PILLOWED BASALTS

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 47.10 | 47.13 | 48.28 | 48.70 | 49.13 | 51.80 | 53.90 | 49.43 | 48.80 |
| $Al_2O_3$ | 15.93 | 18.79 | 13.32 | 15.21 | 16.94 | 17.25 | 19.67 | 16.68 | 13.98 |
| $Fe_2O_3$ | 3.43 | 0.89 | 1.70 | 4.28 | 8.54 | 3.11 | 0.71 | 3.24 | 3.59 |
| $FeO$ | 7.06 | 19.05 | 10.47 | 8.35 | 6.80 | 9.66 | 10.21 | 10.23 | 9.78 |
| $MgO$ | 7.40 | 4.85 | 10.41 | 3.76 | 1.97 | 2.68 | 0.72 | 4.54 | 6.70 |
| $CaO$ | 12.04 | 1.60 | 11.93 | 11.11 | 10.46 | 4.01 | 8.30 | 8.49 | 9.38 |
| $Na_2O$ | 2.98 | 0.95 | 0.78 | 3.23 | 3.32 | 3.88 | 2.78 | 2.56 | 2.59 |
| $K_2O$ | 0.44 | 1.05 | 0.88 | 0.59 | 0.91 | 0.58 | 0.58 | 0.72 | 0.69 |
| $H_2O$ | 1.09 | 4.04 | 1.52 | 0.65 | 2.34* | 4.16 | 1.80 | 2.23 | 1.80 |
| $TiO_2$ | 1.12 | 1.20 | 0.26 | .... | .... | .... | .... | .... | 2.19 |
| $P_2O_5$ | 0.01 | 0.10 | 0.06 | .... | .... | .... | .... | .... | 0.33 |
| $CO_2$ | 1.21 | 0.67 | 0.59 | 2.25 | .... | 3.08 | 0.86 | 1.24 | .... |
| $MnO$ | 0.39 | .... | .... | .... | .... | .... | 0.32 | .... | 0.17 |
| $FeS_2$ | None | 0.22 | .... | .... | .... | .... | .... | .... | .... |
| | 100.20 | 100.54 | 100.20 | 98.13 | 100.41 | 100.21 | 99.85 | 99.36 | 100.00 |

1. Pillowed augite-basalt, Brownridge Township, Kenora district, Ontario. Fe $S_2$ none. $Cr_2O_3$ trace. Sp. gr. 3.021.
2. Gray pillowed basalt, Sandy Lake, Kenora district, Ontario (Satterly, 1938, p. 12). $FeS_2$ 0.22. Sp. gr. 3.089.
3. Pillowed basalt, Sandborn Bay, Sandy Lake, Kenora district, Ontario (Satterly, 1938, p. 11). Sp. gr. 2.916.
4. Ellipsoidal greenstone (basalt), Teck Township, Timiskaming district, Ontario (Burrows and Hopkins, 1914, p. 6).
5. Pillowed andesite, Alexo Nickel Mine, Timiskaming district, Ontario (Baker, 1917, p. 260). *Loss on ignition.
6. Ellipsoidal basalt, Beatty Township, Cochrane district, Ontario (Knight, *et al.*, 1919, p. 21).
7. Amygdaloidal greenstone (pillowed basalt), Teck Township, Timiskaming district, Ontario (Burrows and Hopkins, 1914, p. 6).
8. Average of 1-7 pillowed basalts.
9. Plateau basalt, average of 43 analyses (Daly, 1933, p. 17).

because of the development of chlorite or hornblende as products of metamorphism. Further microscopic work accompanied by numerous analyses is indicated as a solution of this problem of pillowed andesite or pillowed basalt.

## REFERENCES

BAKER, M. B. (1917): Alexo Nickel Mine, Timiskaming district—*Ont. Bur. Mines*, vol. 26, pp. 258-274.

BATEMAN, J. D. (1939): Geology and gold deposits of the Uchi-Slate Lakes area —*Ont. Dept. Mines*, vol. 48, pt. 7, pp. 1-43.

BURROWS, A. G. (1925): The Porcupine gold area—*Ont. Dept. Mines*, vol. 33, pt. 2.

BURROWS, A. G. and HOPKINS, P. E. (1914): The Kirkland Lake and Swastika gold areas—*Ont. Bur. Mines*, vol. 23, pt. 2.

COOKE, H. C., JAMES, W. F., and MAWDSLEY, J. B. (1931): Geology and ore deposits of Rouyn—Harricanaw region, Quebec—*Geol. Surv. Canada*, Mem. 166.

DALY, R. A. (1933): *Igneous Rocks and the Depths of the Earth*—New York.

GEIKIE, Sir A. (1897): *Ancient Volcanoes of Great Britain*—London.

HURST, M. E. (1932): Geology of the Sioux Lookout area—*Ont. Dept. Mines*, vol. 41, pt. 6, p. 6 (photograph).

JOHANNSEN, A. (1932): *A Descriptive Petrography of the Igneous Rocks*, vol. 2—Chicago.

——— (1937): *A Descriptive Petrography of the Igneous Rocks*, vol. 3—Chicago.

KNIGHT, C. W., *et al.* (1919): Abitibi-Nighthawk gold area—*Ont. Bur. Mines*, vol. 28, pt. 2.

LAIRD, H. C. (1935): Geology of the Opeepeesway Lake area—*Ont. Dept. Mines*, vol. 44, pt. 7, pp. 1-30.

LEWIS, J. V. (1914): Origin of pillow lavas—*Bull. Geol. Soc. Am.*, vol. 25, pp. 591-654. (Many references.)

MILLER, W. G. and KNIGHT, C. W. (1914): The Pre-Cambrian geology of southeastern Ontario—*Ont. Bur. Mines*, vol. 22, pt. 2.

MOORE, E. S. (1930): Notes on the origin of pillow lavas—*Trans. Roy. Soc. Canada*, vol. 24, pt. 1, sec. 4, pp. 137-139.

ROBINSON, H. H. (1913): The San Franciscan volcanic field, Arizona—*U.S. Geol. Surv.*, Prof. Paper 76.

SANDBERG, A. E. (1938): Section across Keweenawan lavas at Duluth, Minnesota—*Bull. Geol. Soc. Am.*, vol. 49, pp. 795-830.

SATTERLY, J. (1938): Geology of the Sandy Lake area—*Ont. Dept. Mines*, vol. 47, pt. 7, pp. 1-43.

——— (1939): Preliminary report on the Dryden-Wabigoon area, District of Kenora—*Ont. Dept. Mines* (mimeographed).

SATTERLY, J. (1940): An orbicular gabbro from Tremeer Lake, Kenora district, Ontario—*Univ. Toronto Studies, Geol. Ser.*, no. 44, pp. 75-82.

THOMSON, J. E. (1936): Gold deposits on Shoal Lake (west)—*Ont. Dept. Mines*, vol. 45, pt. 3, pp. 44-53.

WASHINGTON, H. S. (1917): Chemical analyses of igneous rocks—*U.S. Geol. Surv.*, Prof. Paper 99.

WILSON, M. E. (1938): The Keewatin lavas of the Noranda district, Quebec—*Univ. Toronto Studies, Geol. Ser.*, no. 41, pp. 75-82.

WRIGHT, D. G. H. (1922): Black River area—*Ont. Dept. Mines*, vol. 30, pt. 6, pp. 27-62.

# AN OCCURRENCE OF STOLZITE IN THE CARIBOO DISTRICT, BRITISH COLUMBIA

By JOHN S. STEVENSON
*British Columbia Department of Mines*[1]

Stolzite ($PbWO_4$) was found in 1940 by the writer during an examination of the Taylor scheelite prospect on the south-westerly rim of the Snowshoe Plateau, thirty miles south-westerly from the town of Wells. Stolzite is rare and this appears to be the first recorded occurrence of this mineral in Canada.

A detailed description of the few workings on the property has been given by the writer in an earlier publication (1941).

The stolzite, with scheelite and tungstite, occurs in very small amounts in a narrow quartz vein that ranges in width from 1 inch to 4 inches and is exposed for approximately 18 feet before disappearing in a barren vein-shear. Two short branch veins extend for a couple of feet on either side of the main vein. The vein-shear cuts fissile quartzites and sericite schists of the Richfield formation, belonging to the pre-Cambrian Cariboo schists. The nearest igneous rocks lie several miles away.

The vein-matter consists of quartz, pyrite, scheelite, tungstite, and stolzite. A small amount of galena occurs in the branch veins and as widely-scattered grains in the sediments adjacent to the vein. Cube pyrite occurs also in the sediments. The vein possesses a coarsely crystalline texture and in places a coarse banding resulting from development of quartz crystals from the walls. The near-surface section of the vein has been subjected to the action of meteoric waters and a vuggy or honey-comb texture has resulted.

The scheelite is massive to crystalline and well-shaped tetragonal crystals ranging from $\frac{1}{4}$ inch to $\frac{3}{4}$ inch in diameter are common. The unweathered fresh scheelite is resin-coloured, but much of it has oxidized to yellow tungstite. In some instances tetragonal crystals of scheelite have been almost completely replaced by pseudomorphs of tungstite. The nature of the alteration of scheelite to tungstite is plainly discernible when specimens are ground to a flat, fine-grained surface and observed in ultra-violet light. The

---

[1] Published by permission of the Chief Mining Engineer.

scheelite fluoresces brilliantly, and is seen either to be laced by a network of non-fluorescent tungstite veinlets, or to be more completely replaced by large, irregular patches of tungstite.

The stolzite occurs as crusts of minute crystals that line the vugs found within scheelite-tungstite aggregates. The crystals are tetragonal and show well-developed prismatic and pyramidal forms. They range from 0.1 to 1.0 mm. in both length and diameter. The crystal-faces are coated by a thin, brittle film of an earthy-yellow tungstic oxide, probably tungstite, but are themselves white and transparent. The tungstic oxide film is easily chipped off under the binoculars with the point of a fine needle.

The optical properties of the stolzite were determined by immersion of grains in sulphur-selenium melts prepared according to Merwin and Larsen (1912) and observed in monochromatic light of known wave-length from a calibrated spectrometer. A wave-length of 5900Å was used and the $\omega$ and $\epsilon$ indices checked those of melts of 60 per cent and 47 per cent selenium respectively.

The determined indices at 5900Å are as follows:

$$\omega = 2.27$$
$$\epsilon = 2.18$$

These indices check fairly closely with the values of $\omega = 2.269$ and $\epsilon = 2.182$ for stolzite as given by Larsen and Berman (1934, p. 93).

Microchemical tests for lead were made on the mineral and a positive reaction obtained. The writer used the lead iodide test as given by Short (1940, pp. 220-222). The usual method of obtaining a canary-yellow precipitate of tungstic oxide by boiling in mixed acids was used to test for tungsten and positive results obtained. Stolzite is not easily dissolved in ordinary acids and the writer found it necessary to use aqua regia and to reduce the crushed mineral to dryness on a glass slide several times before a soluble salt could be obtained.

Stolzite is generally considered to be an oxidized, or secondary, lead mineral (Hess, 1917, p. 65; Emmons, 1917, p. 430; Lindgren, 1933, p. 854). In this occurrence the stolzite probably resulted from the following processes: (*a*) the action of oxidizing, meteoric waters on the galena of the branch vein and nearby sediments; (*b*) the transportation of the lead as a soluble salt; (*c*) its removal from solution by the scheelite; and (*d*) its deposition as $PbWO_4$, or stolzite, a mineral relatively insoluble in acid waters.

The meteoric waters would be rendered strongly oxidizing by virtue of the oxidation of pyrite in the vein and sediments, and the formation of sulphuric acid and ferric sulphate.

The formation of the supergene mineral stolzite in the Taylor prospect was favoured by the exposure of the closely-associated hypogene minerals, scheelite and galena, to conditions extremely favourable to oxidation and to the formation of secondary minerals.

## ACKNOWLEDGEMENTS

The writer wishes to thank Dr. John F. Walker and Mr. Philip B. Freeland of the British Columbia Department of Mines, who kindly read and criticized the manuscript.

## REFERENCES

EMMONS, W. H. (1917): The enrichment of ore deposits—*U.S. Geol. Surv.*, Bull. 625.

HESS, F. L. (1917): Tungsten minerals and deposits—*U.S. Geol. Surv.*, Bull. 652.

LARSEN, E. S. and BERMAN, H. (1934): The microscopic determination of the nonopaque minerals—*U.S. Geol. Surv.*, Bull. 848.

LINDGREN, W. (1933): *Mineral Deposits*—New York.

MERWIN, H. E. and LARSEN, E. S. (1912): Mixtures of amorphous sulphur and selenium as immersion media for the determination of high refractive indices with the microscope—*Am. Jour. Sci.*, vol. 34, pp. 42-47.

SHORT, M. N. (1940): Microscopic determination of the ore minerals—*U.S. Geol. Surv.*, Bull. 914.

STEVENSON, J. S. (1941): Tungsten deposits of British Columbia—*B.C. Dept. Mines*, Bull. 10.

# THE MINERALOGY OF THE KERR-ADDISON ORE, LARDER LAKE, ONTARIO

By Ellis Thomson
*University of Toronto*

It has always seemed to the writer that a brief study of the minerals at any one mine, carried out both on a qualitative and on an approximate quantitative basis, should reveal interesting results which might be of value from the standpoint of the practical miner. It was with this thought in mind that an investigation was started on the minerals present in the ore of the Kerr-Addison Gold Mines, Ltd.

While more particular attention was directed towards the ore minerals, as examined in polished section, thin sections of each of the specimens were also made and the rock-forming minerals determined under the microscope. In this way some twenty-two specimens were examined in polished and thin sections. As both the recording and the reading of individual descriptions of these sections would be dull and largely unprofitable, the results of the determination of these sections have been set out in tabular form (Table 1), listing those that are present in larger quantities as major constituents and those in smaller quantities as minor constituents. In this connection it should be borne in mind that the terms major and minor are here used in a relative sense only and that in some sections the so-called major metallic constituents are present in comparatively small quantities.

While it is somewhat hazardous to make deductions from the very limited number of sections that were examined from these five orebodies, a careful examination of these results, as set forth in the foregoing tables, seems to lead to the following conclusions. First, and this is subject to no qualification, pyrite is by far the most abundant of the metallic minerals. This is not to say that it occupies a major portion in most of the sections. On the contrary, the metallic constituents in general are present in comparatively small quantities as compared with the rock-forming or gangue minerals. Next in abundance is arsenopyrite which is absent from orebody 19 but present in varying amounts in orebodies

## TABLE 1

### MINERALS IN THE KERR-ADDISON OREBODIES

| Sect. no. | Level | Orebody | Major met. minerals | Minor met. minerals | Major R. F. minerals | Minor R. F. minerals |
|---|---|---|---|---|---|---|
| 6 | 300′ | 9 | pyrite<br>arsenopyrite | chalcopyrite | carbonate<br>quartz | green mica<br>chlorite |
| 13 | 300′ | 10 | pyrite | magnetite | carbonate<br>quartz | green mica |
| 14 | 300′ | 10 | pyrite | magnetite<br>chalcopyrite | carbonate<br>quartz<br>white mica | —— |
| 5 | 500′ | 10 | pyrite<br>arsenopyrite | chalcopyrite<br>gold | carbonate | plagioclase<br>green mica<br>chlorite |
| 18 | 700′ | 10 | pyrite | —— | quartz | carbonate<br>green mica |
| 14 | 175′ | 14 | pyrite | magnetite<br>chalcopyrite<br>gold | quartz | plagioclase<br>carbonate |
| 20 | 300′ | 14 | pyrite | magnetite<br>chalcopyrite | quartz<br>altered plagioclase | carbonate<br>titanite |

TABLE 1 (*Continued*)

| Sect. no. | Level | Orebody | Major met. minerals | Minor met. minerals | Major R. F. minerals | Minor R. F. minerals |
|---|---|---|---|---|---|---|
| 3 | 500′ | 14 | pyrite<br>chalcopyrite | magnetite | altered plagioclase<br>carbonate<br>quartz | titanite |
| 4 | 500′ | 14 | pyrite | chalcopyrite<br>sphalerite | altered plagioclase<br>carbonate<br>quartz | titanite<br>apatite |
| 23 | 700′ | 14 | pyrite<br>arsenopyrite | chalcopyrite<br>pyrrhotite | carbonate<br>quartz | green mica<br>limonite |
| 22 | 1000′ | 14 | arsenopyrite | pyrite | carbonate<br>quartz | green mica<br>limonite |
| 21 | 1300′ | 14 | arsenopyrite | —— | carbonate<br>quartz | green mica<br>limonite |
| 15 | 300′ | 16 | pyrite | chalcopyrite<br>magnetite | carbonate<br>quartz | white mica |
| 7 | 500′ | 16 | pyrite | chalcopyrite | carbonate | quartz |
| 8 | 700′ | 16 | pyrite | chalcopyrite<br>sphalerite | carbonate | quartz |
| 16 | 1000′ | 16 | pyrite | galena | carbonate | quartz<br>chlorite |

TABLE 1 (*Continued*)

| Sect. no. | Level | Orebody | Major met. minerals | Minor met. minerals | Major R.F. minerals | Minor R. F. minerals |
|---|---|---|---|---|---|---|
| 17 | 1300′ | 16 | pyrite<br>arsenopyrite | magnetite | carbonate | quartz<br>chlorite<br>white mica |
| 10 | 175′ | 19 | pyrite | chalcopyrite<br>galena | carbonate<br>quartz | albite<br>chlorite<br>chloritic mica |
| 11 | 300′ | 19 | pyrite | —— | carbonate<br>quartz | albite<br>chlorite<br>chloritic mica |
| 1 | 500′ | 19 | pyrite | chalcopyrite<br>pyrrhotite | white mica<br>chlorite<br>carbonate | quartz<br>titanite |
| 2 | 500′ | 19 | pyrite | sphalerite<br>magnetite<br>gold | carbonate<br>quartz | albite<br>white mica<br>chlorite |
| 12 | 700′ | 19 | pyrite | magnetite<br>chalcopyrite<br>galena | carbonate<br>quartz | albite<br>chlorite<br>chloritic mica |

9, 10, 14, and 16. Chalcopyrite and magnetite, with which is included some ilmenite, follow closely after the arsenopyrite, while the remainder, native gold, sphalerite, galena, and pyrrhotite, are relatively rare in these sections. Of the gangue minerals carbonate and quartz, which are present in almost equal quantities, far outweigh the other gangue minerals. Minor constituents of the gangue, which are present in nearly equal proportions, are plagioclase, chlorite, white mica, and green mica.

This green mica is particularly interesting as it seems to be frequently associated with the native gold. In hand-specimen it has a characteristic light-green colour closely resembling the colour of some specimens of malachite. In thin section it is slightly pleochroic and shows shades of yellow-green and blue-green on rotation of the microscope stage. As such green micas naturally suggest the chrome-bearing varieties it was deemed advisable to carry out a qualitative chemical test for chromium. This was done by Professor L. J. Rogers on 12 grams of mineral powder carefully collected from all the specimens showing this green material. This showed only a trace of chromium, and therefore the mineral is not a chrome mica. The remaining gangue minerals, chloritic mica, titanite, limonite, and apatite, are very rare constituents.

Turning next to a more particular consideration of the four orebodies, 10, 14, 16, and 19, and the variation of metallic mineral content with change of level, some interesting tendencies may be noted. At this point a word of warning must be inserted. As the number of specimens examined from any one orebody at any one level varied from one to two, it might easily be that further investigation with more specimens would change the deductions made from the results of the present investigation. Nevertheless, from the evidence so far available, two or three marked tendencies seem to emerge. The first of these is that arsenopyrite for the most part seems to be characteristic of the lower levels, chiefly from the 700′ level down. This is of course particularly well shown in orebodies 14 and 16 which have been investigated down to the 1300′ level. Exceptions to this general rule are to be found in orebodies 6 and 10 where arsenopyrite occurs as a major constituent at the 300′ and the 500′ levels respectively. In this connection it is noteworthy that this mineral is entirely absent in orebody 19 which was investigated only as far as the 700′ level. The second is that chalcopyrite, which has a considerable range as a minor constituent in many of the sections, seems to disappear below the 700′ level. The third is that pyrite, the most abundant of the metallic minerals present, shows a slight decrease in quantity below the 700′ level. This decrease is more striking in orebody 14 than in orebody 16. Of the other metallic minerals magnetite, with which is included some ilmenite, seems to occur in minor quantities throughout the range from the 175′ level to the 1300′ level.

Turning now to the non-metallic minerals it will be observed that carbonate and quartz are the preponderant gangue minerals. However, an altered plagioclase, which probably represents the residue of a badly-altered country rock, and white mica, are major constituents in some of the sections at the 500′ level or above. It is interesting to note that the white or green micas seem to be present in fair amounts in two out of the three sections where native gold was observed in the polished sections. In orebody 16, on the other hand, where no gold was observed in the five sections examined no green mica was encountered and white mica appeared only as a very minor constituent in two of the sections. This would seem to point to a close association between the micas and the native gold.

To summarize, the trends in mineralization in the orebodies of the Kerr-Addison Gold Mines seem to be as follows:

(*a*) Pyrite is the most abundant of the metallic minerals, although usually present in minor quantities as compared with the gangue minerals. It shows a slight decrease below the 700′ level.

(*b*) Arsenopyrite is the next in abundance of the metallic minerals and with a few exceptions it increases in quantity from the 700′ level down.

(*c*) Chalcopyrite is present as a minor constituent in most sections from the 700′ level up, and it seems to be absent below the 700′ level.

(*d*) Carbonate and quartz are the most abundant gangue minerals.

(*e*) White and green micas may be significant as associates of the native gold as they were present in two out of the three sections where gold was observed.

The writer is fully aware of the fact that the amount of material examined from any one orebody at any one level is inadequate to give a true quantitative picture of the mineralization at this time. Nevertheless some interesting trends have been revealed which might be confirmed by the examination of a larger number of specimens.

In conclusion the writer wishes to express his appreciation of the cordial co-operation extended to him by the management of the Kerr-Addison Gold Mines in making available specimens for microscopic study. He wishes also to thank Professor L. J. Rogers, who found time to carry out a qualitative analysis on the green mica.

# THE WALKER MINERALOGICAL CLUB

## OFFICERS FOR 1940-1941

*Honorary President*............Professor T. L. Walker
*President*...................Professor Ellis Thomson
*Secretary-Treasurer*...............Mr. W. E. Chantler
*Councillors for Ordinary Members*
    For 1939-41..............Mr. W. C. Ringsleben
    " 1939-42.....................Mr. G. E. Steel
    " 1940-3.....................Dr. W. S. Dyer
*Councillor for Department*
    *of Mineralogy*...........Professor M. A. Peacock
*Councillor for Student Members*......Mr. S. A. Forman
*Editor*......................Professor A. L. Parsons
*Past President*.....................Mr. C. W. Drury

The first meeting for the season 1940-1 was held on October 24. From 4 P.M. to 5 P.M. the members gathered in the Royal Ontario Museum of Mineralogy to view a very fine exhibit of cut stones and crystallized minerals loaned by members of the Club. At 5 o'clock they adjourned to the lecture room for the regular meeting.

In the absence of Mr. Drury, Professor Thomson occupied the chair. The Secretary read the report of the Nominating Committee who recommended the following officers:

*President*...................Professor Ellis Thomson
*Secretary-Treasurer*...............Mr. W. E. Chantler
*Councillor for Ordinary Members*
    For 1940-3.....................Dr. W. S. Dyer
*Councillor for the Department*
    *of Mineralogy*...........Professor M. A. Peacock
*Councillor for Student Members*......Mr. S. A. Forman

It was moved by Mr. Steel and seconded by Dr. Meen that the report be accepted.

It was moved by Professor Parsons and seconded by Dr. Peacock that in view of the fact that many student members were engaged on Thursday, both afternoon and evening, in military training, the Council be instructed to arrange meetings for the year on some other day.

It was moved by Professor Parsons and seconded by Mr. Waite that the Secretary-Treasurer be instructed to send out ballots for election of officers and that the poll close on Monday, December 9; that the Council be instructed to canvass the ballot and announce the results thereof at the December meeting.

The Editor, Professor Parsons, gave his report and told of the sending out of the *Contributions to Canadian Mineralogy*. He also announced a radio broadcast at 6.15 by Claire Wallace, advertising the Club and telling of the exhibit by the members in the Museum.

The first speaker of the evening, Mr. G. E. Steel, spoke on the topic "Gem and Crystal Collecting in Ontario." He explained the purpose and benefits of collecting minerals, and told of his experiences in the Michipicoten, Niagara, and Bancroft regions. He pointed out that old government reports had been especially helpful in giving him information in regard to localities.

The second speaker, Mr. G. G. Waite, spoke on "The Cutting of Canadian Gem Stones." He explained the various methods of cutting, and gave some very interesting sidelights on the cutting of diamonds. He showed an exhibit of stones on dop sticks in various stages of cutting and a mathematically designed rest which he had made himself for facetted stones.

Both speakers gave an admirable exposition of their respective topics and it was moved by Professor Parsons that the thanks of the Club be extended to Mr. Steel and Mr. Waite for their most interesting talks and, along with these gentlemen, to Messrs. Horsfall, Titus, Combs, Bullen, and Perry for the special exhibit for the meeting. The thanks of the Club were also extended to Dr. Meen and Mr. Moddle who arranged the exhibit.

After the meeting adjourned, many members stayed to get a closer view of examples of cut stones that the speakers had used to illustrate their lectures.

The second meeting was held on December 17 in the lecture room of the Royal Ontario Museum. Professor Ellis Thomson, the new President elect, occupied the chair.

The Secretary read the results of the ballot for officers who were elected as nominated.

A motion of thanks to the retiring President and officers was moved by Professor Parsons and seconded by Dr. Meen.

It was moved by Professor Parsons and seconded by Dr. Okulitch that the Secretary be authorized to make the necessary arrangements with the bank so that the new President and Secretary-Treasurer might draw cheques on the Club's account.

The speaker of the evening, Mr. W. E. Chantler, gave a talk on "Coloured Photography applied to Mineralogy." His lecture was profusely illustrated with coloured slides and he was ably assisted by Mr. Max Scheerle, of Walter A. Carveth and Co., who contributed many of the coloured photographs, and by Dr. V. B. Meen who showed how coloured photography could be used in conjunction with the petrographic microscope.

Professor Thomson thanked the speakers for their contributions to the efforts of the Club, after which the meeting was adjourned.

The third meeting for the season was held on February 27 in the lecture room of the Royal Ontario Museum with the President in the chair.

The topic for the meeting was "Mineralogical Work and Research at Queen's University." We were first favoured by an account by Professor J. E. Hawley of the results of his most interesting experiments on the synthesis of iron and nickel sulphides (pyrrhotite and pentlandite) which in a more advanced stage was later presented before the Royal Society of Canada in whose *Transactions* it will appear.

The second speaker, Dr. N. W. Buerger, gave an account of controlled temperature *x*-ray technique and described a new camera in which there is a miniature electric furnace into which the specimen is inserted. The furnace is so constructed that the diffraction pattern of the specimen may be obtained while the substance is kept under continuously controlled temperature. By observations at different temperatures, changes in structure and inversion points may be obtained.

The President extended to Professor Hawley and Dr. Buerger the hearty thanks of the Club for their most important contribution to the work of the Club.

The fourth meeting of the year was held in the Mining Building of the University of Toronto on April 24, 1941, at 8 P.M. with President Thomson in the chair.

On motion by Professor Parsons, the President was empowered to appoint a committee to nominate officers for the year 1941-2.

The meeting was then devoted to an account of some of the research that has been carried on in the Department of Mineralogy and Petrography in the University of Toronto during the past year.

Mr. D. A. Moddle gave an account of his work "On the Geometrical, Optical and Structural Crystallography of Augelite."

Mr. F. G. Smith, in his talk on "Precise Measurements of the Cell-edge of Pyrite and Nickeliferous Pyrite," demonstrated a technique for making measurements of a high degree of accuracy on *x*-ray powder photographs, and showed the variation in the cell-edge of pyrite with increasing percentages of nickel.

Professor M. A. Peacock gave an account of the results of his work "On Loellingite and Safflorite"; these minerals are very similar in structure and can hardly be distinguished by physical means.

At the close of the programme the President extended to the speakers the thanks of the Club for a most enjoyable and instructive evening.

The membership of the Club as on June 21, 1941, is as follows:

| | |
|---|---|
| Honorary Members...... | 3 |
| Ordinary Members....... | 355 |
| Student Members........ | 15 |
| Total........... | 373 |

Of these, sixteen members are known to be on active military service and are exempt from dues. In addition the Club has lost two members, Mr. R. H. Combs and Dr. W. S. Dyer, by death, and five members by resignation during the year. There has been a net gain in membership of eighty-three during the year.

## FINANCIAL STATEMENT OF THE WALKER MINERALOGICAL CLUB FROM JUNE 15, 1940, TO JUNE 21, 1941

| | | | |
|---|---|---|---|
| June 15, 1940, Cash on hand and in bank | | $236.33 | |
| RECEIPTS | | | |
| Dues | $316.10 | | |
| Sales of Journal | 24.00 | | |
| Bank interest | .93 | | |
| Exchange less bank charges | 4.26 | | |
| | | $345.29 | |
| | | | $581.62 |
| EXPENDITURES | | | |
| October 25, 1940, University of Toronto Press. | $ 5.43 | | |
| November 22, 1940, Royal Ontario Museum, Zoology | .50 | | |
| November 25, 1940, University of Toronto Press | 12.37 | | |
| December 10, 1940, University of Toronto Press | 269.12 | | |
| December 26, 1940, University of Toronto Press | 5.57 | | |
| January 11, 1941, Secretary, Royal Ontario Museum | .78 | | |
| February 25, 1941, University of Toronto Press | 5.32 | | |
| April 5, 1941, Secretary, Royal Ontario Museum | 1.07 | | |
| April 5, 1941, University of Toronto Press | 18.03 | | |
| April 5, 1941, W. E. Chantler, Postage | 11.00 | | |
| April 8, 1941, Superintendent, University of Toronto | 1.00 | | |
| June 21, 1941, Superintendent, University of Toronto | 2.50 | | |
| June 21, 1941, University of Toronto Press | 6.72 | | |
| | | $339.41 | |
| June 21, 1941, Cash on hand and in bank | | 242.21 | |
| | | | $581.62 |

## BALANCE SHEET

*June 21, 1941*

| | | |
|---|---|---|
| ASSETS | | |
| Cash on hand and in bank | $242.21 | |
| Unpaid dues 1938-9 | 9.00 | |
| 1939-40 | 25.00 | |
| 1940-1 | 54.00 | |
| | | $330.21 |
| LIABILITIES | | |
| Dues paid in advance | $ 46.00 | |
| Surplus | 284.21 | |
| | | $330.21 |

W. E. CHANTLER,
*Secretary-Treasurer.*