# A STUDY OF BARIUM MINERALS FROM THE YUKON TERRITORY

bу

JOSEPH HILTON MONTGOMERY

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#### ABSTRACT

A study of rare barium minerals from the Yukon Territory has resulted in the discovery of at least one and possibly five new species. The present investigation is concerned with one of these, a barium-calcium-iron-alumino-silicate, which is tentatively classed as an inosilicate and named keeleite. The optical and physical properties, a chemical analysis, and the calculation of its formula are presented. The mineral has also been successfully synthesized. An X-ray study of some supergene and alteration products present in the rocks revealed the presence of an interesting mixture of barium-calcium carbonate salts, similar to those obtained as laboratory products. A paragenesis is also presented.

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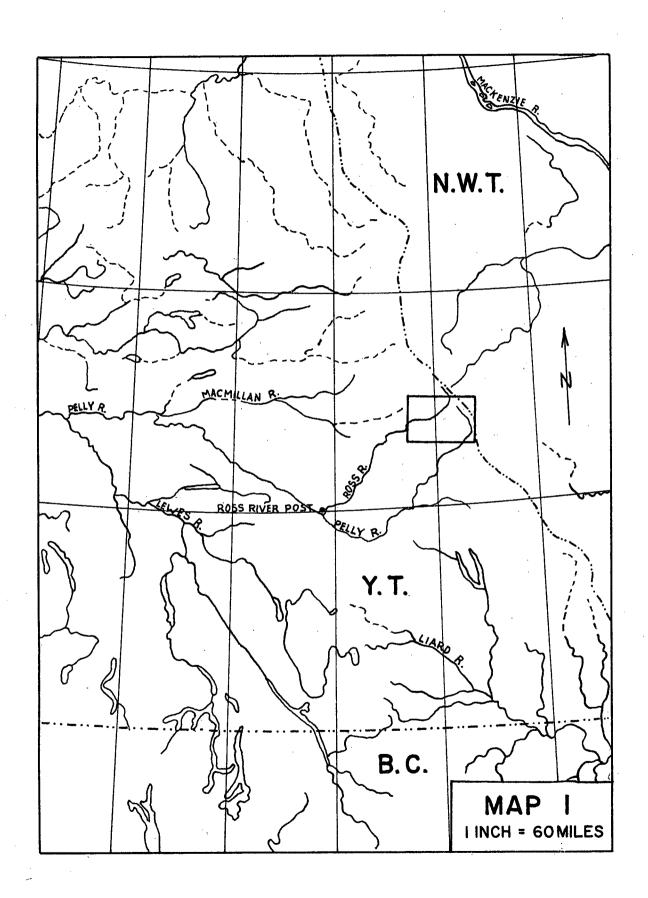
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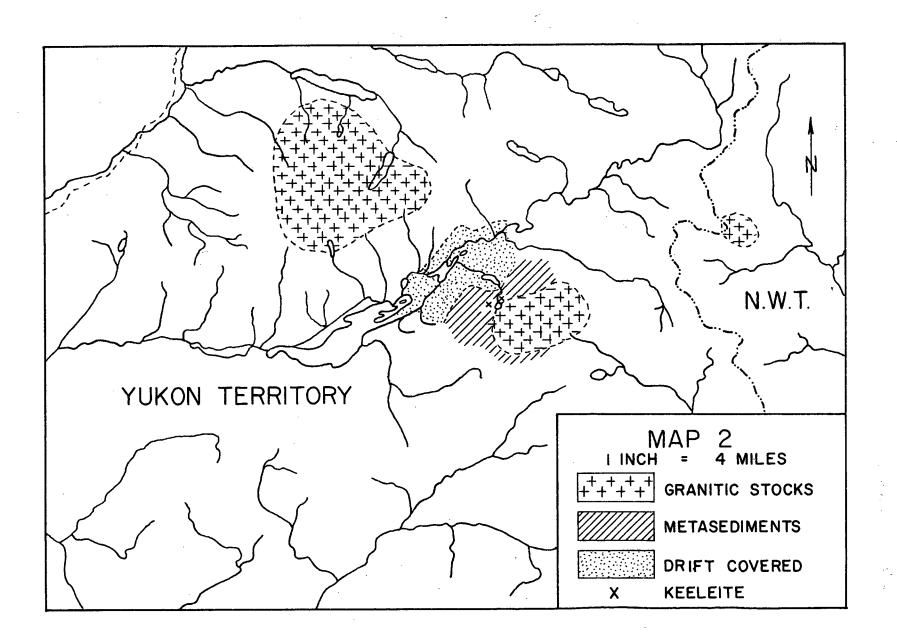
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#### INTRODUCTION

The purpose of this investigation is to describe a new barium mineral, keeleite, which occurs in a contact metasomatic deposit in the Yukon Territory.

The mineral deposit is located on the Sheldon Lake Sheet (Map 105J) near the head-waters of Ross River and about two miles southwest of Gillespite Lake on the Gun group of claims. These claims were staked for their zinc content for the Newmont Mining Corporation of Vancouver,

B.C. in 1957. Map 1 shows the general location of the deposit and Map 2 its exact location and regional geology.

Previous geological work in the area consists only of several reconnaissance operations. Joseph Keele explored the Upper Pelly and Ross Rivers in 1907 and 1908. No further work was done until 1944 when E.D. Kindle made a geological reconnaissance along the Canol Road. In 1958, J.A. Roddick and J.O. Wheeler of the Geological Survey of Canada initiated "Operation Pelly", a geological reconnaissance which includes the Sheldon Lake sheet. It was while in the employ of the Geological Survey of Canada during the 1958 field season that the author collected the specimens on which the present work is based.

The present investigation was suggested by Dr. R.M. Thompson of the University of British Columbia, who identified gillespite (BaFeSi4010) in a specimen sub-

mitted by Mr. Scotty Alan of Newmont Mining Corporation in 1957.

The laboratory work was done at the University of British Columbia in 1959 and 1960.

## REGIONAL GEOLOGY

The area, as shown in Map 2, is characterized by several intrusive stocks which vary in composition from granodicrite to granite. At the contacts of these igneous bodies, the metasediments, which consist of argillites, shales, slates, quartzites, and limestone, have been converted to hornfelses and skarns. Many mineralized zones have been reported associated with some of these granitic stocks. Most of them are simply pyrrhotite impregnations of the thermally metamorphosed rocks, but values in gold, silver, copper and zinc have been obtained in a few.

The contact aureole from which the present suite of specimens was collected surrounds a quartz monzonite stock which is exposed over an area of approximately five square miles. The intruded rocks are steeply dipping to the east, and along the western contact, the bedding is almost vertical. The contact on the north and west sides of the stock dips outward from the stock at an angle of 80 to 85 degrees. The contact aureole is relatively narrow and has an apparent width of 50 to 75 feet.

#### Mineralized Zones

The mineralized zones are lensé-shaped and concordant with the bedding in the metamorphic rocks, and are probably derived from local lime-rich bodies. Two main outcrops of the skarn zone were examined.

The first outcrop is at an elevation of 5,400 feet and is exposed on the west wall of a small cirque. It is a concordant body (0°/60°E) and consists essentially of fine to medium-grained witherite, sanbornite, and hedenbergite. The lense is about 200 feet long and 30 feet thick at its thickest point. The rock on the hanging wall consists of slate, and on the footwall of slate and quartzite. Compositional banding is prominent in the lense, with individual bands varying from 1/2 to 2 inches in thickness and composed of varying concentrations of sanbornite, witherite, and hedenbergite.

The other mineralized zone is in the cirque floor and is exposed largely by open pits which were excavated by Newmont Mining Corporation. This body shows no definite attitude, but in some places, appears almost flat-lying. It consists mostly of fine to medium-grained skarn which contains hedenbergite, gillespite, keeleite, taramellite, and other silicates plus small amounts of sphalerite, chalcopyrite, and pyrrhotite.

## Petrographic Description of the Quartz Monzonite

In hand specimens, the quartz monzonite is leucocratic, medium-grained phaneritic, homophanous, and very slightly porphyritic.

In thin section, plagioclase, orthoclase, quartz, biotite, chlorite, and accessory apatite are evident. The plagioclase is almost all zoned, and occasionally twinned (Carlsbad and Albite twinning). zoning is normal and covers a rather wide range, varying from calcic labradorite (Angg) in the cores to oligoclase ( Ango) on the outside. Orthoclase is present as large anhedral crystals (5mm.) of a slightly porphyritic nature, and which contain many inclusions of small plagioclase crystals and biotite fragments. Both feldspars have been partially sericitized. Quartz occurs as anhedral grains interstitial to the feldspars, and contains inclusions of plagicclase and biotite. A small amount of biotite occurs as subhedral crystals which have been slightly chloritized. Apatite, the only accessory mineral found, is present as minute euhedral crystals.

#### Mode:

Plagioclase - 30% Orthoclase - 30% Quartz - 30% Biotite - 8% Chlorite - 2% Apatite - present.

The wide range of zoning in the plagioclase is indicative of a very rapid change in temperature and/or pressure.

#### KEELEITE

Keeleite (pronounced keel-ite) is named in memory of Joseph Keele, a former officer of the Geological Survey of Canada who made a geological reconnaissance from Ross River Post to the MacKenzie River in 1907-1908.

#### Occurrence:

Keeleite (Ba\(\text{Ca}\_2\)Fe''\(\text{G}'\)Al)\(\text{Al}\)\(\text{2}\)(SiO\(\text{3}\)\(\text{12}\)) is found in a contact metasomatic deposit adjacent to a porphyritic quartz monzonite stock. It occurs as a massive, crystalline constituent of skarns which have developed in original limestone bodies adjacent to the igneous contact. The mineral assemblage includes keeleite, barite, hedenbergite, quartz, and adite, taramellite ((Ba,Ca,Na)\(\text{4}\)(Fe'\,Mg) Fe''2 Ti(Si\(\text{4}\)O\(\text{12}\)(OH)\(\text{4}\), gillespite (BaFeSi\(\text{4}\)O\(\text{10}\)), sanbornite (BaSi\(\text{205}\)), chalcopyrite, witherite, double carbonate salts of barium and calcium, and four other minerals which may be new species.

## Physical Properties:

In hand specimen, keeleite is massive, crystalline, and intimately mixed with its associated minerals and alteration products. It possesses three poorly developed cleavages which are usually evident only in thin section. The mineral is colorless to pale yellow, has a hardness of 6, a specific gravity of 3.51, and fuses at 3 to a weakly magnetic bead. It possesses a vitreous lustre and conchoidal fracture very similar to that of quartz. The alteration products of keeleite include a fibrous blue pleochroic mineral, a sericitic mineral, a pale yellow fibrous pleochroic mineral, a yellow isotropic mineral, and a yellow-brown mineral. These minerals also result from the alteration of gillespite or sanbornite and are more fully described in the section on alteration products. Specimens which were collected from the surface are coated with a yellow, earthy material and a white crust of barium-calcium carbonate salts and opal.

## Optical Properties:

The indices of refraction of keeleite were determined with immersion oils and the optical orientation by the universal stage method. The values given for the optic angle and cleavage angles were corrected using Federow's diagram. The optical orientation is represented in Figure 1 and the optical properties are as follows:

Color - colorless in thin section.

Form and Cleavage - subhedral to euhedral tabular crystals with two prismatic cleavages which make an angle of 44° with each other, and one pinacoidal cleavage. All the cleavages are poorly developed.

## Indices of Refraction -

$$n_x = 1.643 \pm .003$$
  
 $n_y = 1.645 \pm .003$   
 $n_z = 1.649 \pm .003$ 

Birefringence -  $n_z - n_x = .006$ 

Extinction - Parallel to elongation of crystals.

Orientation - length fast or length slow because of the tabular nature of the crystals.

Twinning - The twin plane is parallel to the elongation of the crystal.

Optic Angle and Sign - the figure is biaxial positive with 2V = 47°.

 $\frac{\text{Dispersion}}{r} - \text{rhombic, very strong with}$ 

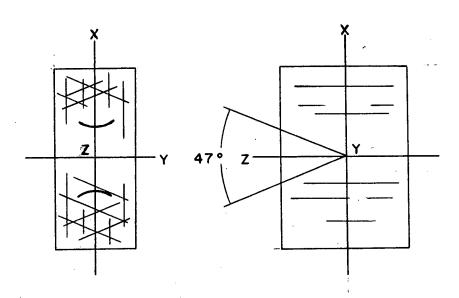


Figure 1. Optic Orientation of Keeleite.

# Chemical Analysis and Calculation of Formula:

Keeleite is intimately mixed with its alteration products and the minerals gillespite, quartz, taramellite, hedenbergite, andradite, sulfide minerals, and carbonates. It was therefore impossible to find any specimens pure enough for analysis. Consequently, it was necessary to

resort to grinding, screening, magnetic separation, heavyliquid separation and finally, hand-picking under the binocular microscope. The following procedure was found to be satisfactory.

Hand specimens which contained relatively large amounts of keeleite were crushed to 1/4 inch size. cleanest of these fragments were ground and screened to obtain a +80 and -60 mesh fraction. This fraction was then passed through a Franz Isodynamic Separator set at a 25 degree tilt and a 15 degree cant. An amperage of 0.425 removed most of the gillespite, the blue alteration product, and the sulfides while the keeleite and mixed grains remained behind in the non-magnetic fraction. The mixed grains were removed by hand-picking under the binocular microscope. A very small amount of quartz was removed by gravity separation in bromoform. The results of a spectrographic analysis made on a portion of the sample are presented in Table 1.

| Major | Intermediate | Minor | Trace |
|-------|--------------|-------|-------|
| Ва    | Ca           | Mg    | В     |
| Si    | Äl           | Zn    | Be    |
|       | Fe           | Mn    | Ti    |
|       |              | Na    | Zn    |
|       |              | Sr    |       |

Table 1. Spectrographic Analysis of Keeleite.

A sample of keeleite weighing about 0.8 grams was submitted for chemical analysis to H.V. Sharples, G.S. Eldridge & Co., Vancouver, B.C. The results appear in Table 2 with calculations for a chemical formula.

| Oxide                          | %     | Corr.% | Mol. Wt. | Mol.P. | Mol.<br>Ratio | Th.%  |
|--------------------------------|-------|--------|----------|--------|---------------|-------|
| BaO                            | 34.16 | 34.33  | 153.36   | .223   | 6.021         | 34.07 |
| CaO                            | 6.25  | 6.28   | 56.08    | •112   | 3.024         | 6.23  |
| SiO <sub>2</sub>               | 40.50 | 40.70  | 60.06    | .667   | 18.009        | 40.03 |
| Al <sub>2</sub> 0 <sub>3</sub> | 3.53  | 3.55   | 101.94   | .0348  | 0.949         | 3•77  |
| Fe0 *                          | 11.97 | 12.03  | 71.58    | .1665  | <b> </b>      |       |
| MnO                            | 0.57  | 0.57   | 70.90    | .0080  | 6.048         | 15.90 |
| MgO                            | 1.46  | 1.48   | 40.32    | .0365  | 0.040         |       |
| Zn0                            | 1.05  | 1.06   | 81.38    | •0130  | 1             |       |
| so <sub>3</sub>                | tr.   |        |          |        |               |       |
|                                | 99•49 | 100.00 |          |        |               |       |

\*Total iron calculated to FeO

Table 2. Chemical Analysis and Calculation of Formula for Keeleite.

In calculating the formula, the following procedure was used. Neglecting the trace of sulfur, the metal oxide percentages were corrected to bring the total to 100%. and their molecular proportions calculated by dividing the corrected percentages by their appropriate molecular weights. It was then necessary to decide which elements were substituting for others and which were essential

to the crystal structure. Since barium and silicon oxides are the major components, they were considered essential The alumina could have been added to the silica, as aluminum commonly replaces silicon in many silicate struc-It was, however, retained as an essential contures. stituent because there are not sufficient monovalent cations present to compensate for the deficiency in positive charge which would result, and also because the near perfect balance of SiO2:BaO = 3:1 would be upset. The oxides of ferrous iron, manganese, magnesium, and zinc when added together gave a molecular proportion of 0.224 which is equivalent to that of barium oxide and one-third that of silica. High valence manganese might substitute for aluminum, but again the balance of molecular proportions would be destroyed if MnO were calculated in with alumina. Calcium oxide is also considered an essential constituent. Although the ionic radius of calcium (0.99) is sufficiently small to enable it to substitute for barium (1.34), the size difference is greater than the 15% limit generally accepted for ion substitution. Furthermore, the ratio CaO:BaO = 1:2 suggests that calcium occupies an essential position in the lattice. Calcium might also substitute in part for ferrous iron (0.74), but this possibility is rejected for the same reasons stated above.

The smallest near whole numbers are obtained when the molecular proportions are multiplied by a factor of 27. The derived formula is thus 6Ba0.3Ca0.6Fe0.Al<sub>2</sub>0<sub>3</sub>. 18Si0<sub>2</sub>, or in the more conventional manner - Ba<sub>6</sub>Ca<sub>3</sub>Fe<sub>6</sub>Al<sub>2</sub> (Si0<sub>3</sub>)18.

Although microlites of keeleite were obtained from a mixture of this composition, the formula, Ba6Ca3Fe6Al2(SiO3)18 is not the correct formula. The reasons for this statement will be discussed fully in the section on synthesis.

## Synthesis of Keeleite:

In order to test the possibility of synthesizing keeleite by direct fusion of the constituent oxides, the natural mineral was fused to a glass. An X-ray powder photograph of the fused material showed that the structure had been completely destroyed. The mineral was then placed in an evacuated silica tube and annealed at 850°C for 24 hours. The resultant product was not completely crystallized, probably owing to the relatively short annealing period, but microlites in radiating groups were scattered throughout the glass. An X-ray powder photograph of this product proved the crystals to be keeleite. Thus, no hydrous or gaseous constituents are present.

The main difficulties encountered in synthesizing keeleite were the instability of its constituent oxides, the problem of a suitable container, and the necessity of maintaining a neutral atmosphere during fusion and crystallization to prevent the oxidation of ferrous iron. Bowen and Schairer<sup>3</sup> experienced difficulty in controlling and defining the state of oxidation of iron in their work on

the system FeO - SiO<sub>2</sub>. They found that even in vacuums to 0.000\(\psi\) mm. Hg, the ferrous iron oxidized. A solution was obtained by using iron crucibles in a nitrogen atmosphere. The iron crucibles served to keep the iron in the ferrous state, but small amounts of iron were added to the melt by reaction with the crucible. Schairer and Yagi\(^4\) successfully crystallized silicates in the system FeO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> by folding pieces of the glass in iron foil, sealing them in evacuated silica tubes, and heating at temperatures below the solidus for several days or weeks. Several charges of keeleite composition were fused in iron crucibles, but without success.

Barium oxide is available as chemically pure material, but is somewhat hygroscopic and consequently does not keep well. Ferrous oxide is very unstable and oxidizes rapidly to a mixed material on standing. The product used in the synthesis of keeleite was obtained by heating ferrous oxalate (FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O) under vacuum to expel the carbon dioxide and water. The return to atmospheric pressure must be gradual to prevent combustion of the unstable product. It appeared to be homogeneous and composed entirely of black ferrous oxide. Since calcium oxide is very hygroscopic, calcium was added in the form of CaSiO<sub>3</sub> which was made by fusing calcium carbonate and silica. Alumina and silica were easily obtained in pure form and offered no problem.

The containers with which the writer was most successful were Vitreosil tubes which were sealed under vacuum to obtain an atmosphere as close to neutral as possible.

The oxides were weighed out in appropriate amounts to make a 10 gram charge. Only 2 grams were required for the fusion, but greater accuracy is obtained by weighing the larger amounts. The oxides were ground in a mortar and thoroughly mixed. The mixture was then placed in a silica tube and heated gently under vacuum to expel any moisture which may have been picked up during grinding and mixing. The tube and contents were gradually heated to a red heat, then sealed by melting in an oxygengas flame and twisting off the end of the tube. The charge was then fused at 1350°C in a "Glow-Bar" furnace and kept in the fused state for one hour. Some corrosion took place on the inside wall of the tube, but apparently a small amount of excess silica is not detrimental to the formation of keeleite. The stability of keeleite in excess silica is suggested by the occurrence together of keeleite and quartz in nature. The tube was then opened. A piece of the charge, now a silicate glass, was chosen from the center of the melt and placed in another silica tube, which was evacuated and heated at 850°C for 48 hours. The purpose of the change was to allow most of the surface area of the silicate glass to be out of contact with the tube in order

to prevent reaction during the long period of annealing. The product obtained was apparently entirely crystalline and composed of fine prismatic crystals. An X-ray powder photograph of this material proved it to be keeleite with a small amount of contaminating quartz. A comparison of X-ray data for synthetic keeleite, natural keelite and and fused, annealed natural keelite is presented in Table 3. Optical determinations were not made on the synthetic product because of its extremely fine grain, and a specific gravity determination was not made because of the possible presence of undetected glass or free silica.



Plate I. Laths of keeleite (crossed nicols). X75.

Table 3. X-ray Data for Natural Keeleite, Fused-Annealed Keeleite, and Synthetic Keeleite.

| Natural   | Keeleite   | Fused-A                                  | nnealed  | Synthetic  | Keeleite   |                              |  |
|---|--|--|--|--|--|------------------------------|--|
| (UBC X  | (2528)   | Natural Keeleite<br>(UBC X2704)          |  | Natural Keeleite                                   |  | Watural Keeleite (UBC X2947) |  |
| I   | đ  | I  | d  | I  | d  |                              |  |
| 184 15 3 10 10 11 1 7 12222 182222312 1 32224 1 31853 | 6.51<br>5.99<br>4.21<br>3.88<br>3.45<br>3.16<br>3.00<br>2.46<br>3.00<br>2.10<br>2.20<br>2.30<br>2.11<br>2.07<br>2.02<br>2.10<br>2.02<br>2.10<br>2.03<br>1.83<br>1.70<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67<br>1.67 | 1-2-120-10-12-1-2-1-2-12-2-2-2-2-2-2-2-2 | 5.99<br>4.25<br>3.90<br>3.45<br>3.16<br>2.85<br>2.47<br>2.24<br>1.965<br>1.838<br>1.778<br>1.610<br>1.540<br>1.480 | - 18733356 - 0871-18181812111123 - 142-181-1823342 | 6.955383 q q q 1.555383 q q 1.555383 q q 1.5555383 q q q q q q q q q q q q q q q q q q |                              |  |

q - possible quartz lines.

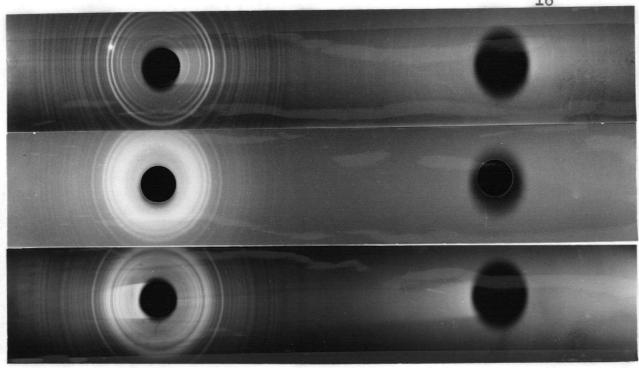


Plate II X-ray Powder Photographs of Keeleite.

Top - Keeleite, Y.T. - UBC X2529 Cu/Nio.

Center - Fused-Annealed Keeleite, Y.T.-UBC X2704 Cu/NiO.

Bottom - Synthetic Keeleite - UBC X2968 Cu/Nio.

The data above show that almost every line on the X-ray film for natural keeleite is also present for the synthetic material. The extra lines marked (q) are attributed to the presence of a small amount of quartz. The remaining discrepancies in spacing and intensities are believed due to preferred orientation of microlites in the synthetic material. Levin and Ugrinic were confronted by a similar problem in their work on the system BaO-B2O3-SiO2. They found that X-ray diffraction data

for their silicates varied both in the lines present or absent, and in their relative intensities. They attributed the discrepancies to preferred orientation.

It was stated previously that, although crystals were obtained from a melt of composition Ba6Ca3Fe6Al2(SiO3)18, that this formula was incorrect. In the analysis given in Table 2, only total iron was determined and that calculated to FeO. However, a later sample submitted to the same analyst for the determination of ferrous and ferric iron showed that 8.32% FeO and 4.16% Fe2O3 are present in the mineral keeleite. A new chemical formula was calculated on the basis of these results as shown in Table 4.

| Oxide   | %   | Mol.Wt.  | Mol.<br>Prop.  | Mol.Ratio                           |
|---|---|--|--|-------------------------------------|
| BaO<br>CaO<br>SiO2<br>Al2O3<br>Fe2O3<br>FeO<br>MnO<br>MgO<br>ZnO<br>SO3 | 34.16<br>6.25<br>40.50<br>3.53<br>4.16<br>8.32<br>0.57<br>1.46<br>1.05<br>tr. | 153.36<br>56.08<br>60.06<br>101.94<br>159.16<br>71.58<br>70.90<br>40.32<br>81.38 | .223<br>.111<br>.674<br>.035<br>.026<br>.116<br>.008<br>.036 | 4.014<br>1.998<br>12.132<br>} 1.098 |

Table 4. Revised Calculation of Keeleite Formula.

The calculation of the formula was done in the same manner as shown in Table 2, except that  $Fe_2O_3$  was added to  $Al_2O_3$ . A factor of 18 was used to obtain the molecular ratios. The resulting formula is  $\mu BaO.2CaO.$ 

3FeO.(FeAl)<sub>2</sub>O<sub>3</sub>.12SiO<sub>2</sub> or Ba<sub>4</sub>Ca<sub>2</sub>Fe'<sub>3</sub>(Fb',Al)<sub>2</sub>(SiO<sub>3</sub>)12. The question of how keeleite crystals could be obtained from the original formula may be answered readily by comparing the percentages of oxides contained in the two formulas as shown in Table 5.

| Oxide  | Ba6Ca3Fe6Al2(SiO3)18 | Ba4Ca2Fe3(Fe,A1)2(SiO3)12 |
|--|----------------------|---------------------------|
| BaO  | 34.07 %              | 33.70                     |
| CaO  | 6.23                 | 6.16                      |
| FeO  | 15.9                 | 11.80                     |
| Al <sub>2</sub> 0 <sub>3</sub> or Fe <sub>2</sub> 0 <sub>3</sub> | 3•77                 | 8.74                      |
| Si0 <sub>2</sub>   | 40.03                | 39•59                     |

Table 5. Comparison of Oxide Percentages in the Two Calculated Formulas.

The percentages of the oxides of barium, calcium and silicon are close enough in the two formulas to allow crystallization of keeleite from either. The discrepancy between FeO and (Al,Fe)2O3 in the two formulas indicates that oxidation of the ferrous iron must certainly have taken place to allow the development of keeleite crystals in the melt. Any oxides in excess over those required for the formation of the compound may have combined with silica and remained in the glassy state.

In the course of syntheses of keeleite, one additional compound was obtained from the composition 5BaO.2FeO.Fe<sub>2</sub>O<sub>3</sub>.1OSiO<sub>2</sub>. The crystals obtained were dark

brown, platy, and distributed in coarse radial groups.

X-ray powder diffraction data for this compound is given in Table 6. It does not resemble any known mineral or previously reported silicate compound.

| UBC 2   | 2852  | Fe/Mn0 |   |  |
|---|---|--------|---|--|
| I<br>10<br>9<br>7<br>2<br>6<br>3<br>1<br>2<br>1 | d 3.98 3.73 3.28 3.08 2.98 2.77 2.67 2.28 2.22 2.16 | I -    | d<br>2.12<br>1.989<br>1.964<br>1.870<br>1.803<br>1.706<br>1.640<br>1.595<br>1.495 |  |

Table 6. X-ray Data for Ba5Fe2Fe2 (Si03)10



Plate III X-ray Powder Photograph of the Compound 5Ba0.2Fe0. Fe<sub>2</sub>O<sub>3</sub>.10SiO<sub>2</sub>. UBC X2858 Cu/NiO.

# Alteration Products of Keeleite:

The alteration products of keeleite include several minerals which are of hydrothermal origin and several which have been identified as carbonates of barium and calcium. The hydrothermal replacement minerals have been designated by letters.

The most abundant alteration product is Mineral C, a finely fibrous blue mineral which is strikingly pleochroic in brilliant blues and pale yellows. This mineral also appears as an alteration of gillespite and was first reported by Schaller in 1929 in association with gillespite from Dry Delta, Alaska. It is also found in the gillespite from Mariposa County, California. This occurrence was described by Pabst in 1943.

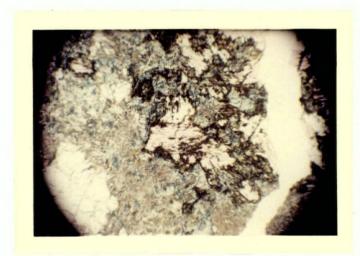


Plate IV Mineral C (blue) which has replaced gillespite (pink) and keeleite (white). X75.

Its optical properties are as follows.

mixed with a sericitic mineral.

Color - blue, strongly pleochroic with x - colorless to pale yellow. y - pale blue. z - dark blue.

Form - Fibrous aggregates, intimately

Cleavage - one cleavage parallel to the length of the crystal, and one poorly developed cleavage or parting perpendicular to the first.

Indices of Refraction -

 $n_x = 1.659 \pm .005$ 

 $n_v = 1.704 \pm .005$ 

 $n_z = 1.704 \pm .005$ 

Birefringence -  $n_z - n_x = .045$ .

Extinction - parallel.

Orientation - the fast ray is parallel to the length of the crystal.

Twinning - no twinning observed.

Optic Angle and Sign - the figure is biaxial negative with 2Vx~45°.

Dispersion - strong, with r < v.

A possible optical orientation for Mineral C is presented in Figure 2.

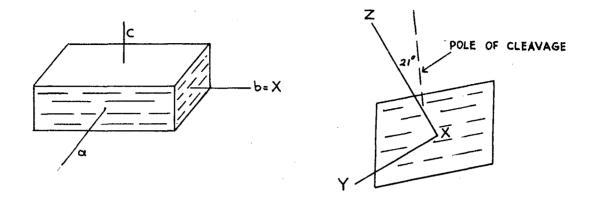


Figure 2. Possible Optic Orientation of Mineral Co.

Several X-ray powder photographs were taken on picked grains, and although the mineral is finely divided and intimately mixed with keeleite and gillespite, thus making it difficult to obtain pure material, the same X-ray pattern was obtained on different material. X-ray data is presented in Table 7.

|                  | Mineral C  | - ивс х2646 |  |
|------------------|--|-------------|--|
| I                | đ  | I           | đ  |
| 3047-127-1244454 | 3.62<br>3.35<br>3.21<br>3.04<br>2.81<br>2.59<br>2.47<br>2.26<br>2.11<br>2.04<br>1.888<br>1.821 | うって         | 1.689<br>1.664<br>1.605<br>1.540<br>1.508<br>1.417<br>1.377<br>1.318<br>1.291<br>1.258 |

Table 7. X-ray Data for Mineral C.



Plate V X-ray Powder Photograph of Mineral C, Yukon Territory, UBC X2646 Cu/NiO.

A closed tube test of Mineral C yielded a small amount of water. The blue color of the mineral disappeared and a yellow-brown, granular residue remained in the tube. A spectrographic analysis of Mineral C showed the presence of minor boron and lithium in addition to those elements detected in keeleite and gillespite. The results are tabulated in Table 8.

| Major                  | Minor   | Trace                            |
|------------------------|---------|----------------------------------|
| S <b>i</b><br>Fe<br>Ba | B<br>Li | Mn<br>Mg<br>Al<br>Ca<br>Cu<br>Zn |

Table 8. Spectrographic Analysis of Mineral C.

Mineral C, as stated previously, replaces both keeleite and gillespite. In gillespite, it follows the prominent basal cleavage, but in keeleite, the replacement has no preferred direction. The alteration product is commonly a heterogeneous product consisting of Mineral C and finely fibrous aggregates of a sericitic-looking material.

Another alteration product of keeleite, which has been designated Mineral D, is a brilliant yellow, isotropic mineral or mineraloid which also replaces gillespite. It may be the mineral mentioned by Rogers in 1932 as occurring with sanbornite from Mariposa County, California. This mineral occurs only in very small amounts and consequently, sufficient material for X-ray or spectrographic analyses was unavailable. Another yellow mineral, which occurs as fibrous aggregates cutting through keeleite, has a slight birefringence and may be still another distinct species. This mineral is designated Mineral F and is shown in Plate VI.

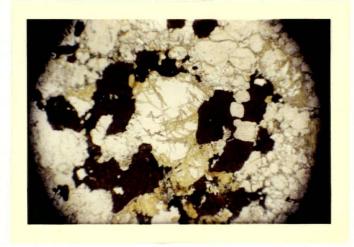


Plate VI Mineral F(yellow) cutting keeleite (white). The dark brown mineral is sphalerite.

A fourth mineral, which has been designated Mineral E, is relatively common as scattered anhedral grains throughout the mineral, sanbornite.

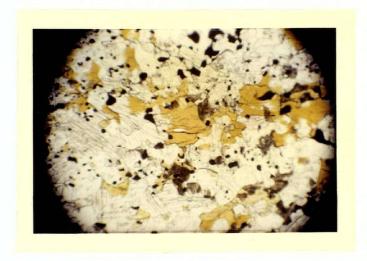


Plate VII Mineral E (yellow) which has formed by alteration of sanbornite (white). X75

It also occurs in small amounts in minute cracks traversing keeleite and its associated minerals. It is strikingly pleochroic in brilliant orange and yellow. A spectrographic analysis showed the presence of major quantities of manganese and titanium in addition to those elements contained in keeleite, gillespite, and sanbornite. The results of the spectrographic analysis are presented in Table 9.

| Major                      | Minor | Trace          |
|----------------------------|-------|----------------|
| Ba<br>Si<br>Fe<br>Mn<br>Ti | Ca    | Mg<br>Sn<br>Al |

Table 9. Spectrographic Analysis of Mineral E.

A closed tube test of Mineral E yielded detectable amounts of water. No color change took place as in the blue mineral. X-ray powder photographs of the mineral occurring with sanbornite and of that occurring in cracks traversing keeleite gave identical patters. The results are tabulated in Table 10.

| Mineral E - UBC X2548 Cu/NiO                    |   |                    |  |  |
|---|---|--------------------|--|--|
| I   | đ   | I                  | đ  |  |
| 10<br>2<br>4<br>2<br>8<br>2<br>2<br>3<br>1<br>1 | 4.42<br>3.75<br>3.531<br>2.91<br>2.74<br>2.60<br>2.49<br>2.21 | ଧ ଧ ଧ୍ୟକ୍ଷଧ ଧ ର କଳ | 2.16<br>2.09<br>2.04<br>1.965<br>1.910<br>1.824<br>1.749<br>1.650<br>1.427 |  |

Table 10. X-ray Data for Mineral E.

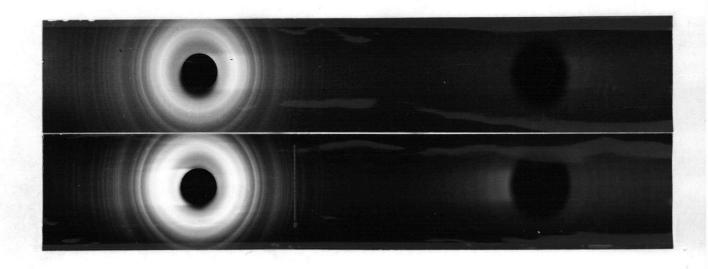


Plate VIII X-ray Powder Photographs
of Mineral E.

(Top) Mineral E associated with
sanbornite, Yukon Territory,
UBC X2548 Cu/NiO

(Bottom) Mineral E associated with
keeleite, Yukon Territory,
UBC X2976 Cu/NiO

In addition to the replacement minerals described in the foregoing section, several unusual supergene minerals are present on the specimens which were exposed to weathering. The first of these commonly occurs as a very fine-grained ocherous powder in thin coatings on keeleite. Where keeleite is mixed with appreciable quantities of gillespite, it gives an unusual red and yellow mottled appearance to the rocks. An X-ray powder photograph of this material showed only a few very weak lines

indicating a poorly crystalline material.

The surfaces of many of the specimens are coated with layers of botryoidal white material, most of which was determined as witherite and opal. Some of it is apparently a more complex mixture of barium-calcium carbonates. A comparison of an X-ray powder photograph of this material with those of alstonite, the orthorhombic barium-calcium carbonate and of barytocalcite, its monoclinic dimorph, showed that the supergene product was However, a comparison with neither of these minerals. X-ray diffraction data of synthetic alstonite and barytocalcite 10 proved almost certainly that the supergene product is a mixture of both these carbonate salts. A comparison of X-ray diffraction data for the white supergene coating, synthetic barytocalcite, and synthetic alstonite is given in Table 11.

| White Coating<br>UBC X2973     |   | Synthetic Baryto-<br>calcite. A.S.T.M.<br>Index Car 1-0770 |  | Synthetic Alston-<br>ite. A.S.T.M.<br>Index Card 3-0322 |  |
|--------------------------------|---|--|--|---|--|
| I                              | d   | I  | đ  | I   | d  |
| 1 7 3 10 6 6 6 6 5 3 - 2 - 1 1 | 4.48<br>3.99<br>3.69<br>3.14<br>2.56<br>2.15<br>1.933<br>1.642<br>1.563<br>1.475<br>-<br>1.337<br>1.318 | 10 10 10 10 13 35 1 34445<br>10 10 10 13 13 15 1 34445     | 3.96<br>3.16<br>2.54<br>2.14<br>2.00<br>1.94<br>1.57<br>1.51<br>1.47<br>1.39<br>1.34<br>1.32<br>1.28 | 7502<br>1002<br>10477<br>1227<br>52-5725                | 4.51<br>3.68<br>3.60<br>2.52<br>2.13<br>2.98<br>1.64<br>1.46<br>1.46<br>1.46<br>1.33<br>1.22 |

Table 11. Comparison of X-ray diffraction data of White Coating, Synthetic Barytocalcite and Synthetic Alstonite.

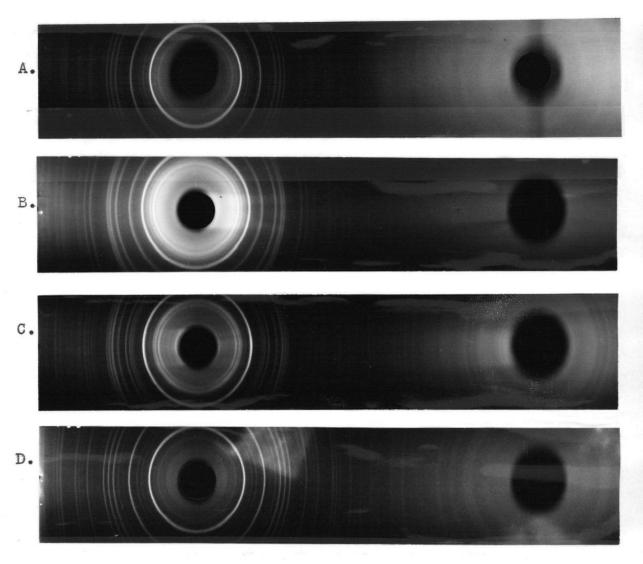


Plate IX X-ray Powder Photographs of Barium-Calcium Carbonates.

- A. Witherite, Yukon Territory UBC X2492 Cu/NiO.
- B. Mixed Carbonates, Yukon Territory UBC X2973 Cu/NiO.
- C. Barytocalcite, Cumberland UBC X2982 Cu/NiO.
- D. Alstonite, Cumberland UBC X2988, Cu/NiO.

A comparison of X-ray patterns B, C, and D in Plate IX shows that the supergene mixed carbonates (B) bear no similarity to either barytocalcite (C) or alstonite (D). However, the X-ray data for synthetic alstonite and barytocalcite are strikingly close to that of the supergene coatings.

This anomoly is explained later in the section on paragenesis.

## Associated Minerals:

The minerals which occur in association with keeleite include the minerals which are found usually in contact limestones such as garnet, quartz, and hedenbergite. latter mineral occurs commonly in such mineral deposits with chalcopyrite. It is present in the keeleite assemblage with pyrrhotite and marcasite. Occasional very small grains of magnetite were noted in some thin sections. The remaining minerals found in the keeleite assemblage are very rare barium silicate minerals, most of which are known only in one or two localities, and many of which are probably new species. Those minerals which occur as alteration products have been described in the section on that subject. Three additional minerals which occur with keeleite are taramellite (BahFeFeZTi(SiO3)8(OH)1\*, gillespite (BaFeSi<sub>1010</sub>), and sanbornite (BaSi<sub>2</sub>05).

Taramellite occurs as small equant grains or relict crystals disseminated throughout keeleite, quartz, gillespite, and Mineral C.

<sup>\*</sup> A new formula which is proposed for the mineral taramellite and which is based on a chemical analysis published by Mazzi<sup>ll</sup> in 1957.



Pleochroic colors of taramellite (brown and yellow) in keeleite X75.



Relict crystals of taramellite in quartz and keeleite X75.



Taramellite (yellow) in gillespite (pink) X75.

The following optical properties were determined in thin sections or on individual grains in immersion oils:

Color -

Pleochroic yellow to deep brown.

x - light yellow.

y - light yellow.

z - dark brown.

Form and Cleavage -

short prismatic grains with square cross-sections; one poor cleavage parallel to the length of the crystal.

Indices of Refraction - n ~ 1.76

Birefringence -

not determined, strong pleochroism interfered.

Extinction - parallel.

Twinning - no twinning observed.

Optic Angle and Sign the figure is biaxial positive with
2V = 350.

Dispersion - strong, with r > v.

These properties compare closely with those of taramellite from the type locality, Candoglia, Italy.

A spectrographic analysis of taramellite from the Yukon locality gave the results which are presented in Table 12.

| Major                | Minor         | Trace  |
|----------------------|---------------|--|
| Ba<br>Fe<br>Ti<br>Si | Mg<br>Ca<br>B | Mn<br>Sn<br>Cu<br>Ag<br>Pb<br>Zn<br>Na<br>Al |

Table 12. Spectrographic Analysis of Taramellite (Ross River, Y.T.)

Taramellite also occurs in sanbornite (BaSi<sub>2</sub>O<sub>5</sub>) specimens from Mariposa County, California. In 1932, Rogers<sup>8</sup> mentioned an unknown brown pleochroic mineral which occurred in that assemblage. In addition, Schaller<sup>6</sup>, in 1929, described a pleochroic yellow to deep brown mineral occurring in gillespite specimens from Dry Delta, Alaska. Specimens from the locality were examined by the author, and it is believed that this mineral is also taramellite. The X-ray diffraction data for material from Mariposa and Yukon is compared to that for taramellite from the type locality in Table 13.

| Candog<br>UBC X2         | lia, Italy<br>546 Fe/MnO  | Ross River, Y.T. UBC X2479 Fe/MnO   |  | Mariposa Cty, Calif.<br>UBC X2689 Fe/MnO |   |
|--------------------------|---|---|--|--|---|
| I                        | đ   | I   | đ  | I  | đ   |
| 128425206633242211334224 | 7.00<br>6.12<br>3.86<br>3.69<br>3.48<br>3.33<br>3.16<br>3.02<br>2.59<br>2.48<br>2.40<br>2.31<br>2.18<br>2.06<br>1.989<br>1.878<br>1.744<br>1.699<br>1.638<br>1.524<br>plus severa | 1<br>18<br>10<br>35<br>1<br>1<br>1<br>1<br>2<br>1<br>3<br>1<br>3<br>1<br>1<br>1<br>1<br>1<br>1<br>1<br>1<br>1<br>1<br>1 | 6.92<br>6.19<br>3.90<br>3.69<br>3.18<br>3.03<br>2.80<br>2.61<br>2.49<br>2.32<br>2.18<br>2.08<br>1.998<br>1.881<br> |  | -<br>6.09<br>3.88<br>3.70<br>3.34<br>3.19<br>3.04<br>2.81<br>2.81<br>2.998<br>1.815<br>1.798<br>1.798<br>1.798<br>1.758<br>1.758<br>1.538 |

Table 13. X-ray data for Taramellite.

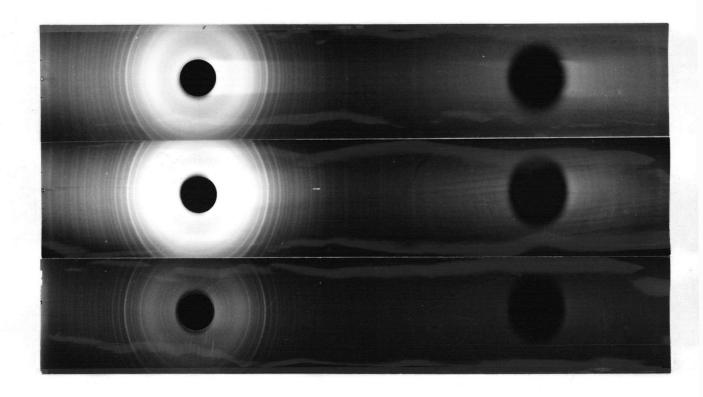


Plate XI X-ray Powder Photographs of Taramellite.

(Top) Taramellite, Candoglia, UBC X2546 Fe/Mno.

(Center) Taramellite, California, UBC X2689 Fe/Mno.

(Bottom) Taramellite, Y.T., UBC X2570 Fe/Mno.

In 1957, Florenzo Mazzi calculated the formula, (Ba,Ca, Na) 4 (Fe,Mg)Fe2Ti(Si492)(OH) 4 for the mineral taramellite from a chemical analysis on material dried at 110°C. A recalculation by the author based on the same analysis gave the formula Ba4FeFe2Ti(SiO3)8.(OH)4. This formula fits the analysis better, and is suggested as the correct one. The method of calculation is presented in Table 14.

| Oxide                                      | 8%  | Mol.Wt.   | Mol.P.   | Mol. Ratio                           |
|--|---|---|--|--------------------------------------|
| SiO23<br>TiOO3<br>FeO MgO BaO CaO Ng2O K2O | 33.9<br>7.7<br>12.2<br>3.7<br>0.8<br>37.5<br>1.1<br>0.8<br>0.1<br>2.1 | 60.06<br>79.9<br>159.7<br>71.58<br>40.32<br>153.36<br>56.08<br>62.0<br>94.2<br>18.0 | .565<br>.096<br>.076<br>.052<br>.020<br>.245<br>.020<br>.013<br>.001 | 7.91<br>1.34<br>1.06<br>1.01<br>3.90 |

Table 14. Chemical Analysis of Tara-mellite and Calculation of its Formula.

A factor of 14 was used to obtain the molecular ratios. The formula which resulted from the above calculations is 4Ba0.Fe0.Fe<sub>2</sub>0<sub>3</sub>.Ti0<sub>2</sub>.8Si0<sub>2</sub>.2H<sub>2</sub>0 or in the more conventional manner, Ba<sub>4</sub>FeFe<sub>2</sub>Ti(Si0<sub>3</sub>)<sub>8</sub>(OH)4. The mineral taramellite is therefore classed as an inosilicate.

Gillespite (BaFeSi4010) occurs as crystalline masses in a skarn consisting of hedenbergite, andradite, quartz, keeleite, and lesser amounts of the other minerals described under other sections. Gillespite is a deep rose red color, has a prominent micaceous cleavage, a pearly lustre, a hardness of 3, and a specific gravity of 3.33. Its alteration products are the same minerals which occur with keeleite.

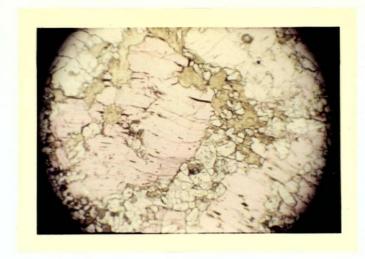


Plate XII Gillespite (pink), keeleite (white), and taramellite (brown). X75

The optical properties of gillespite are as follows:-

Color - strongly pleochroic
0 = pale pink to colorless
E = deep rose red.

Form and Cleavage - anhedral grains with a perfect basal cleavage.

Indices of Refraction -  $n \sim 1.62$ .

Birefringence - very weak.

Extinction - parallel.

Twinning - no twinning observed.

Optic Angle and Sign - the figure is uniaxial negative.

These properties compare closely with those obtained for gillespite from the two localities, Dry Delta, Alaska and Mariposa County, California. The mineral was first discovered by W.T. Schaller (1929)<sup>6</sup> in a single specimen from a glacial moraine at the head of Dry Delta, Alaska Range, Alaska. The mineral assemblage in the Alaska specimen is very similar to that in the

Ross River specimens except that keeleite is absent in the former. The only other previously reported locality for gillespite is near Incline, Mariposa County, Calif.

No keeleite has been reported from that locality, but the remainder of the assemblage is almost identical to that of the Ross River specimens.

Table 15, which follows, presents a comparison of X-ray data of specimens from California and Yukon Territory.

| Ross River, Y.T.<br>UBC X2188 Fe/MnO |   | Mariposa Cty., Calif.<br>UBC X2187 Fe/MnO |   |
|--------------------------------------|---|---|---|
| I                                    | đ   | I   | đ   |
| 1884 - 288 - 23고당등등교교 기교육의 교육        | 7.89<br>4.42<br>3.99<br>3.49<br>3.49<br>2.76<br>2.65<br>2.29<br>2.25<br>1.940<br>1.877<br>1.771<br>1.534<br>1.478 | 1083-287123元kk・11123元kmk3                 | 7.95<br>4.44<br>4.03<br>3.40<br>3.40<br>3.77<br>2.57<br>2.39<br>2.00<br>1.881<br>1.774<br>1.6543<br>1.479 |

Table 15. X-ray Data for Gillespite.

A spectrographic analysis of gillespite from the Yukon occurrence is presented in Table 16.

| Ba Al Mg Fe B Si Ca Mn Cu |
|---------------------------|
| Ti<br>Na                  |

Table 16. Spectrographic Analysis of Gillespite.

Sanbornite (BaSi<sub>2</sub>0<sub>5</sub>) occurs as fine-grained crystals (0.5 to 2.0 mm.) associated with Mineral E, quartz, hedenbergite, and witherite. It was not found with keeleite, but occurred in an outcropping lense about 100 feet away from the igneous contact. Sanbornite was recognized in thin section by its characteristic optical properties which are as follows:-

Color - colorless in thin section.

Form and Cleavage - anhedral grains with a perfect basal cleavage.

Birefringence -  $n_z - n_x = .020$ .

Extinction - inclined extinction, small angle.

Orientation - the fast ray is parallel to the cleavage.

Twinning - no twinning observed.

Optic Angle and Sign - the figure is biaxial negative with 2V = 65°.

Dispersion - not observed.

A spectrographic analysis of sanbornite from the Yukon Territory is presented in Table 17.

| Major    | Minor    | Trace                      |
|----------|----------|----------------------------|
| Ba<br>Si | Na<br>Al | Fe<br>Cu<br>Ca<br>Mn<br>Mg |

Table 17. Spectrographic Analysis of Sanbornite.

Sanbornite was first described by Rogers (1932)<sup>8</sup> from specimens found in Mariposa County, California, and the crystal structure was determined by Douglass (1958)<sup>12</sup> using specimens from the same locality. X-ray powder data on specimens from Yukon Territory is compared with that obtained by Douglass on Mariposa sanbornite in Table 18.

Table 18. X-ray Data for Sanbornite.

|  |  | 3  | · · · · · · · · · · · · · · · · · · ·  |
|--|--|--|--|
| Ross R<br>UBC X2   | iver, Y.T.<br>557 Cu/NiO   | Mariposa Cty., Calif.<br>R.M. Douglass                   |  |
| I  | đ  | I  | đ  |
| 43 8 - 1810 - 172 - 1 - 12 - 1 - 13 - 15 - 1 - 14 - 1 - 12 - 13 - 14 | 6.81<br>5.04<br>3.97<br>3.38<br>3.21<br>3.09<br>2.72<br>2.57<br>2.30<br>2.23<br>2.15<br>2.02<br>1.914<br>1.848<br>1.794<br>1.689<br>Plus several r | 30<br>100<br>100<br>100<br>100<br>100<br>100<br>100<br>1 | 6.79<br>5.08<br>3.97<br>3.82<br>3.422<br>3.422<br>3.422<br>3.980<br>2.980<br>2.9888<br>2.5741<br>2.36<br>2.317<br>2.36<br>2.130<br>2.130<br>2.130<br>2.109<br>2.038<br>2.130<br>2.109<br>2.035<br>1.990<br>1.815<br>1.793<br>1.736<br>1.799<br>1.690 |

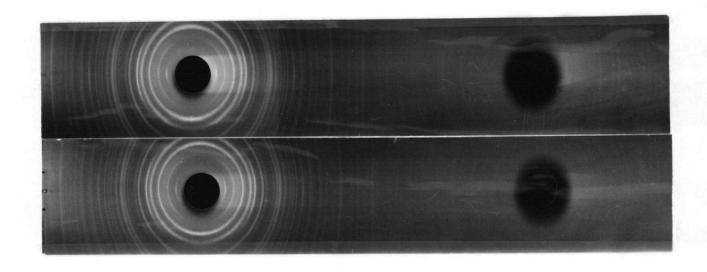


Plate XIII X-ray Powder Photographs of Sanbornite.

(Top) Sanbornite, California, UBC X2556 Cu/Nio.

(Bottom) Sanbornite, Y.T., UBC X2557 Cu/NiO.

## Paragenesis:

The mineral deposit is of the contact metasomatic class and has resulted from the intrusion of a quartz monzonite stock into country rock consisting of slates, phyllites, limestones, and other low grade regionally metamorphosed types. The metasomatic replacement was favoured in lime-rich lenses present in the original metasediments. High temperatures are indicated by textural relationships in the sulfides, and rapid cooling is suggested by the presence of relict mineral crystals and pseudomorphs in the skarn assemblage. Rapid changes

in temperature and/or pressure are also suggested by the extreme zoning in plagioclase feldspars ( $An_{66}$  to  $An_{20}$ ) within the intrusive body.

Relationships between all the minerals in the assemblage were not observed in thin section, but sufficient evidence was present to allow some conclusions to be drawn regarding the paragenesis of the deposit. For convenience, the paragenetic sequence is divided into three parts or phases. This division does not necessarily imply that there were three separate periods of mineralization. It is quite probable that deposition was continuous, and that the various minerals were deposited in a definite sequence controlled by rapid changes in pressure, temperature and the composition of the metasomatic fluids.

The first phase was one of temperature increase which resulted in the formation of garnet and pyroxene. Some specimens consist essentially of euhedral crystals of pyroxene and anhedral garnet in keeleite and its alteration products. The garnet has partially replaced hedenbergite, but the relationship of these minerals to keeleite is obscured by the alteration of keeleite and the later addition of sulfide minerals which replace all silicates.

The second phase consisted of the metasomatic addition of barium, titanium, silica, iron, and minor boron, lithium, and manganese. This metasomatism resulted

in the formation of gillespite, keeleite, sanbornite, and taramellite. Taramellite is believed to be early because it commonly occurs as relict crystals which have been partly replaced by other minerals. In one specimen. where taramellite occurs with keeleite and quartz, almost every grain of the taramellite is so badly corroded as to leave only a bare network of the original mineral. Keeleite and gillespite may have been contemporaneous, but in one section, the former mineral was seen to cut across a crystal of gillespite, and further, gillespite crystals are sometimes seen to butt up against the more euhedral keeleite grains. The relative position in the paragenesis of sanbornite is not known because it occurs separately in a lense-shaped bed about 100 feet from the main deposit. The alteration products are also included in this phase although they are all obviously later. The presence of water and such elements as boron and lithium, which were detected in Mineral C, suggests a rather late stage in the process, quite probably following even the deposition of sulfides. Mineral C, the blue fibrous mineral, has replaced gillespite along its prominent basal cleavage and its grain boundaries. some instances, it has completely replaced that mineral. Keeleite is apparently less susceptible to replacement by Mineral C, but has also been replaced to a relatively moderate extent. Mineral D has replaced keeleite in many sections, particularly in those sections containing

sulfide minerals. This relationship suggests that the replacement of gillespite and keeleite by Mineral D was contemporaneous with sulfide emplacement. The only mineral seen to replace sanbornite was Mineral E. The latter occurs as anhedral grains along the grain boundaries of sanbornite. It also occurs in small quantity in minute fractures in the keeleite-gille spite rocks.

The third phase is considered to embrace the emplacement of the sulfide minerals. Chalcopyrite sphalerite, pyrrhotite, and marcasite have replaced all silicates. Chalcopyrite occurs as exsolved rims and blebs within and around sphalerite grains giving an "emulsion" or "mottled" texture. Some laths of chalcopyrite are oriented in the (111) or (100) planes of sphalerite. According to Edwards 13, these textures represent all stages in the arrested diffusion of exsolution chalcopyrite to the grain boundaries of its sphalerite host. He states also that this texture is the result of high temperature deposition and rapid cooling, and that the temperature of unmixing is 350 - 450 degrees C. Pyrrhotite exhibits mutual boundaries with the other sulfides and is probably contemporaneous with them, possibly deposited from a complex solid solution with complete segregation of pyrrhotite from the other Marcasite has replaced pyrrhotite to a consulfides. siderable extent along fractures. Edwards states that replacement of pyrrhotite by marcasite may be caused by

a change in the pH and temperature of the residual mineralizing solutions.

A number of barite veins occur in the immediate vicinity of the mineral deposit. They range in width from two or three inches to one foot and may be up to several hundred feet long. The barite occurs in very well-formed crystals up to three inches in length or in plates forming a boxwork. These veins cut across the country rock and the mineralized zones, and are probably the result of a very late stage in the paragenesis.

The formation of white, supergene barium-calcium carbonates as coatings on the surface rocks is attributed to precipitation from solutions at or very near the surface. The reason for this belief is found in the very close resemblance of the supergene carbonates to synthetic barium-calcium carbonates. The synthetic salts were precipitated from solutions of CaCl<sub>2</sub>, BaCl<sub>2</sub>, and Na<sub>2</sub>CO<sub>3</sub> and called synthetic barytocalcite and alstonite even though their X-ray patterns do not resemble those of the natural minerals. It is therefore suggested that the synthetic materials and those natural minerals occurring as supergene coatings on keeleite are polymorphs of alstonite and barytocalcite with the composition BaCa(CO<sub>3</sub>)2. It is further suggested that natural alstonite and barytocalcite may form only under considerable pressures of CO<sub>2</sub>.

## CONCLUSIONS

A new mineral, keeleite, is described. The chemical formula, based on chemical analysis and synthesis, is Ba<sub>4</sub>Ca<sub>2</sub>Fe'<sub>3</sub>(Al,Fe)<sub>2</sub>(SiO<sub>3</sub>)12. The mineral is tentatively classed as an inosilicate. Optical properties suggest that the mineral is orthorhombic.

The minerals designated by the letters C, D, and E are probably new species.

Three new localities for taramellite have been proven by X-ray and optical determinations. In addition to the type locality, Candoglia, Italy, taramellite occurs in the Yukon Territory, in Mariposa County, California, and in the material from Dry Delta, Alaska. Sanbornite, previously a one-locality mineral, has also been shown to occur in the Yukon Territory.

The presence of supergene barium-calcium carbonates in the deposit, which are similar to salts obtained synthetically, suggests a natural occurrence of minerals of composition BaCa(CO<sub>3</sub>)<sub>2</sub>. If this assumption is true, the minerals are probably polymorphs of alstonite and barytocalcite.

A new formula, Ba<sub>4</sub>FeFe<sub>2</sub>Ti(SiO<sub>3</sub>)<sub>8</sub>(OH)<sub>4</sub>, is suggested for the mineral taramellite.

A paragenetic sequence based on present evidence has been presented. It is quite possible that this paragenesis will be revised with a more exhaustive examination

of the field relationships. The author had the opportunity to spend only one day on the property, and it is probable that careful investigation would reveal better crystallized material, additional mineral species, and more evidence for a paragenetic sequence.

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