## HUTTONITE, A NEW MONOCLINIC THORIUM SILICATE

# A. Pabst, University of California, Berkeley, California.

# WITH AN ACCOUNT OF ITS OCCURRENCE, ANALYSIS, AND PROPERTIES

C. Osborne Hutton, Stanford University, California.

#### ABSTRACT

The name huttonite is given to a mineral of composition ThSiO<sub>4</sub>, isostructural with monazite. It has been isolated in minute grains from beach sands of South Westland, New Zealand. It is monoclinic; sp. gr. 7.1;  $\alpha$ =1.898,  $\beta$ =1.900,  $\gamma$ =1.922; dispersion r < v, moderate;  $2V=25^{\circ}$ ; Y||b, Z near c; colorless to very pale cream. Space group  $C_{2h}^{5}$ — $P2_{1}/n$ ;  $a_{0}$ =6.80Å,  $b_{0}$ =6.96,  $c_{0}$ =6.54,  $\beta$ =104°55′; cell content 4(ThSiO<sub>4</sub>).

### X-RAY EXAMINATION

Professor Hutton turned over to the writer a portion of a new mineral which he had concentrated from the sands of Gillespie's Beach, South Westland, New Zealand. The material received consisted of several hundred minute grains, none more than  $0.2\,\mathrm{mm}$ . in maximum dimension, weighing a few hundredths of a gram altogether. The grains were all anhedral, mostly bounded by more or less conchoidal fractures and in part by smoother surfaces taken to be parting or rudimentary cleavage. These surfaces were invariably found to be parallel to the b-axis. Several somewhat platy fragments were found to be flattened nearly parallel to the (100) plane. The distinct cleavage nearly normal to the acute bisectrix, reported by Hutton, was only seen in a few grains.

From this material both powder and single crystal diffraction patterns were obtained. The single crystal patterns required very long exposures due to the minute size of the crystals. All crystals had to be mounted with the aid of the polarizing microscope. The first fragment was mounted with the rotation axis parallel to a prominent parting surface and at right angles to Y. When finally adjusted after several trial runs the rotation axis proved to be the c axis. Thereafter it was possible to set crystals for rotation on a desired axis fairly well if fragments could be found yielding a suitable interference figure. Eventually rotation and zero and first layer Weissenberg patterns were obtained on both the c and b axes.

The cell dimensions, obtained from the best lines of the indexed powder pattern and checking closely with values derived from single crystal patterns, calibrated by quartz, are:

 $a_0 = 6.80 \pm 0.03$  Å  $b_0 = 6.96 \pm 0.03$  Å  $\beta = 104^{\circ}55' \pm 10'$  Y||b  $c_0 = 6.54 \pm 0.03$  Å. Z near c. All patterns were made with copper radiation. The wave length of the unresolved  $\text{Cu-K}_{\alpha}$  radiation was taken to be 1.542 Å.

Assuming a cell content of 4(ThSiO<sub>4</sub>) the calculated density becomes 7.18, to be compared with the value 7.1, found by Hutton.

Systematic extinctions unambiguously indicate the space group to be  $C2_h^5 - P2_1/n$ .

These findings show the thorium silicate found and described by Hutton to be a new mineral, distinct from the tetragonal form of this compound long familiar as the mineral thorite. It is proposed to call this new mineral huttonite.

#### Systematic Relations

The cell dimensions of huttonite are very close to those of monazite, the cell content is analogous and the space group is the same. The optical character and orientation are also similar. As may be seen from Tables 1 and 2 and from Fig. 1 there is close correspondence of both rotation and powder patterns of the two minerals.

Reports on the cleavage of monazite are conflicting, but {100} and {001} are sometimes recognized as cleavage or parting directions. Rather obscure or imperfect cleavage or parting close to these directions is also noted in huttonite.

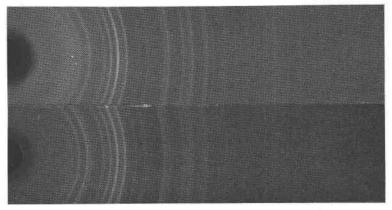


Fig. 1. Powder patterns CuK rays, Ni filter. Camera diameter 114.6 mm. Top—monazite; bottom—huttonite.

The finding of a close relation of huttonite to monazite has been foreshadowed to some extent by the finding of a substantial ThO<sub>2</sub> and SiO<sub>2</sub> content in many monazites. In a number of cases these "impurities" are present in the proportion of ThSiO<sub>4</sub>. This led some mineralogists to the supposition that these monazites were contaminated by mechanical

Table 1. Comparison of Zero Layer Lines of c-Axis Rotation Patterns of Huttonite and Monazite

| Huttonite  Gillespie's Beach, South Westland, New Zealand |           |         | Monazite‡ "Turnerit," Perdatsch, Switzerland, as reported by S. von Gliszczynski in Table 1, Zeit. Kr., 101, 4 (1939). |           |         |  |
|---|-----------|---------|--|-----------|---------|--|
| Tiew Zealand  |           |         |  |           |         |  |
| hkl   | Intensity | Spacing | hkl  | Intensity | Spacing |  |
| 020   | 1+        | 3.49    | 020  | W         | 3.45    |  |
| 200   | 10        | 3.29    | 200  | st        | 3.32    |  |
| 120   | 8         | 3.10    | 120  | m         | 3.11    |  |
| 210   | 3         | 2.98    |  |           |         |  |
| 220   | 1         | 2.400   | 220  | W         | 2.405   |  |
| 310   | 2         | 2.095   | 310  | w         | 2.115   |  |
| 320   | 5         | 1.859   | 320  | st        | 1.862   |  |
| 040   | 3         | 1.749   | 040  | m         | 1.742   |  |
| 140   | 4         | 1.692   | 140  | m         | 1.686   |  |
| 400   | 5         | 1.647   | 400  | st        | 1.657   |  |
| 410*  | 6         | 1.600   | 410, 330?  | st        | 1.614   |  |
| 240   | 2         | 1.546   | 240  | w         | 1.545   |  |
| 340, 150†   | 1         | 1.370   | 340, 150   | mst       | 1.369   |  |
| 510*  | 4         | 1.293   | 510  | st        | 1.301   |  |
|   |           |         | 250?   | W         | 1.285   |  |
| 520   | 2         | 1.233   | 520  | st        | 1.237   |  |
| 440   | 1 —       | 1.199   | 440  | m         | 1,203   |  |
|   |           |         | 350  | vw        | 1.180   |  |
| 060   | 2         | 1.169   | 060  | m         | 1.164   |  |
| 530*  | 5         | 1.148   | 530, 160   | st        | 1.151   |  |
| 260*  | 3         | 1.102   | 260, 600   | m         | 1.099   |  |
| 610   | 5         | 1.085   | 610  | st        | 1.089   |  |
| 450   | 2         | 1.068   | 450  | m         | 1.068   |  |

<sup>\*</sup> Indexing assured by comparison with Weissenberg pattern.

admixture of thorite. Brögger (1906), however, considered the ThSiO<sub>4</sub> as being a part of the monazite itself and spoke of the "homoiomorpher Verbindung (ThO)SiO<sub>3</sub>," which may be considered to have been found in the new mineral huttonite.

The structure of monazite has been investigated by Kokkoros (1942) and the structure of artificial CePO<sub>4</sub> has been reported by Mooney (1948). These investigators agree as to cell dimensions, cell content and space group but arrive at different parameters. Since the original paper by Kokkoros has not been accessible to the writer and the findings of

<sup>†</sup> Not observed on Weissenberg pattern.

<sup>‡</sup> Gliszczynski lists angles, from which spacings have been derived for this table. The question marks with certain indices have been copied from Gliszczynski. The beta spots in his table are here omitted.

TABLE 2. COMPARISON OF POWDER PATTERNS OF HUTTONITE AND MONAZITE

| Huttonite Gillespie's Beach S. Westland, N. Z. |          |            |                  | Monazite<br>near Chochi-wan, southern Korea* |             |                |  |
|--|----------|------------|------------------|--|-------------|----------------|--|
| Intensities                                    | Spacings |            |                  | Spac   | Intensities |                |  |
| estimated                                      | obs.     | calc.†     | $hkl\ddagger$    | calc.  | obs.        | estimated      |  |
| 3  | 5.29     | 5.28       | 101              | 5.13   | 5.23        | 4              |  |
| _  | -        | 4.80       | 110              | 4.78   | 4 70        | 4              |  |
| 5  | 4.71     | 4.69       | 011              | 4.67   | 4.72        | 4              |  |
| 6  | 4.23     | 4.19       | <b>T11</b>       | 4.13   | 4.17        | 6              |  |
| 4  | 4.08     | 4.08       | 101              | 4.11   | _           | _              |  |
| 4  | 3.53     | 3.52       | 111              | 3.54   | 3.52        | 5              |  |
|  | -        | 3.48       | 020              | 3.50   |             |                |  |
| 6  | 3.29     | 3.29       | 200              | 3.29   | 3.31        | 7              |  |
|  | -        | 3.16       | 002              | 3.12   |             | <u>0=</u> /    |  |
| 8  | 3.09     | 3.07       | 120              | 3.08   | 3.09        | 10             |  |
| -  | 10-0     | 3.05       | 021              | 3.05   |             | -              |  |
| 3  | 2.98     | 2.98       | 210              | 2.98   | 2.99        | 2              |  |
| -  | -        | 2.96       | 211              | 2.92   |             | <del></del>    |  |
| -  | -        | 2.89       | T21              | 2.88   |             | -              |  |
| -  | 0.00     | ∫2.89      | <b>T</b> 12      | 2.83   | 2.88        | 7              |  |
| 7  | 2.89     | 2.88       | 012              | 2.86∫  | 2.00        | ,              |  |
|  | -        | 2.65       | 121              | 2.66   |             | -              |  |
| 3  | 2.65     | 2.64       | $\bar{2}02$      | 2.57   | 2.61        | 2              |  |
| -  |          | 2.48       | 211              | 2.45   |             | <u></u>        |  |
| 3  | 2.48     | 2.47       | $\overline{2}12$ | 2.41   | 2.45        | 3 (b)          |  |
| 1  | 2.44     | 2.44       | 112              | 2.45   | 2.43        | 3 (0)          |  |
| -  | -        | 2.39       | 220              | 2.40   | _           | _              |  |
| 4  | 2.19     |            |                  |  | 2.19        | 4              |  |
| 2  | 2.156    |            |                  |  |             |                |  |
|  |          |            |                  |  | 2.139       | 6              |  |
| 3  | 2.110    |            |                  |  |             |                |  |
| 4  | 1.953    |            |                  |  | 1.969       | 5              |  |
|  |          |            |                  |  | 1.963       | 1              |  |
| 3  | 1.893    | 2)         |                  |  | 1.899       | $\binom{2}{b}$ |  |
| 2  | 1.857    | <i>b</i> ) |                  |  | 1.875       | 0)             |  |
| 2  | 1.810    |            |                  |  | 1.800       | 2              |  |
| 2  | 1.784    |            |                  |  | 1.766       | 4              |  |
| 4  | 1.749 (  | <i>b</i> ) |                  |  | 1.746       | 6              |  |
| 2  | 1.692    |            |                  |  | 1.695       | 4              |  |
| 2  | 1.646    |            |                  |  | 1.651       | 1 —            |  |
|  |          |            |                  |  | 1.630       | 1-             |  |
| 3  | 1.603    |            |                  |  | 1.605       | 1              |  |
| 3  | 1.550    |            |                  |  | 1.541       | 4              |  |

<sup>\*</sup> Kindly furnished by Mr. C. W. Chesterman.

<sup>†</sup> Spacings obtained by the graphical method of Peacock (Zeit. Kr., 100, 93–103, 1938) from cell dimensions given in Table 3.

<sup>‡</sup> The sequence of indexed lines in the table is determined from huttonite.

Mooney have been reported only in a preliminary fashion it is not easy to arrive at an opinion on the merits of the conflicting results. Nevertheless it can be asserted with great confidence that huttonite is isostructural with monazite.

| TABLE 3. CELL DIMENSIONS OF SOME MATERIALS ISOMORPHOU | S |
|---|---|
| WITH MONAZITE AND ZIRCON                              |   |

| Material                                   | $a_0$              | $b_0$                | Co                   | β       | Cell<br>volume | Reference                      |
|--|--------------------|----------------------|----------------------|---------|----------------|--------------------------------|
| Huttonite, ThSiO <sub>4</sub><br>Monazite† | 6.80 Å             | 6.96 Å               | 6.54 Å               | 104°55′ | 299            | Pabst, 1950                    |
| (Ce, La)PO <sub>4</sub>                    | 6.76               | 7.00                 | 6.42                 | 103 10  | 296            | Parrish, 1939                  |
| LaPO <sub>4</sub>                          | $6.89\mathrm{\AA}$ | $7.05  \mathrm{\AA}$ | 6.48 Å               | 103 34  | 306            | Mooney, 1948                   |
| CePO <sub>4</sub>                          | $6.76\mathrm{\AA}$ | $7.00  \text{\AA}$   | $6.44  \mathrm{\AA}$ | 103 38  | 296            | Mooney, 1948                   |
| $PrPO_4$                                   | 6.75  Å            | $6.94\mathrm{\AA}$   | $6.40\mathrm{\AA}$   | 103 21  | 292            | Mooney, 1948                   |
| $NdPO_4$                                   | 6.71 Å             | $6.92  \mathrm{\AA}$ | $6.36  \text{\AA}$   | 103 28  | 287            | Mooney, 1948                   |
| $BiPO_4$                                   | 6.78               | 6.99                 | 6.45                 | 104     | 297            | Zemann, 1949                   |
| Crocoite, PbCrO <sub>4</sub>               | 7.108              | 7.410                | 6.771                | 102 27  | 353            | v. Gliszczynski,<br>1939       |
| Zircon, ZrSiO <sub>4</sub>                 | 6.60               |                      | 5.88                 |         | 256            | Wyckoff & Hen-<br>dricks, 1927 |
| Thorite,* ThSiO₄                           | 6.315              |                      | 5.667                |         | 226            | Boldyrev et al., 1938          |
| Xenotime, YPO <sub>4</sub>                 | 6.88               |                      | 6.013                |         | 285            | Vegard, 1927                   |
| $YVO_4$                                    | 7.126              |                      | 6.197                |         | 314            | Broch, 1933                    |
| CaCrO <sub>4</sub>                         | 7.25               |                      | 6.34                 |         | 333            | Clouse, 1932                   |

Note:—Where units are not specified in this table they are in doubt though probably kX.

A number of substances isostructural with monazite are listed in Table 3. According to Mooney (1948) the phosphates of lanthanum, cerium and neodymium are "dimorphic," existing also in an hexagonal form. However, she states that "the presence of zeolitic water . . . is probably necessary to stabilize the structure." Under these circumstances this is not strictly a case of dimorphism. ThSiO<sub>4</sub>, on the other hand, is now known to be dimorphous, having representatives in both the monazite and zircon groups.

The more familiar tetragonal form of ThSiO<sub>4</sub>, thorite, is nearly always metamict. Vegard (1916) failed to observe any x-ray diffraction in it. An indexed powder pattern of thorite from the Langesundfjord, Norway, has, however, been published and cell dimensions given by Boldyrev, Mikheiev, Kovalev and Dubinina (1938) as well as by Mikheev and

<sup>\*</sup> See text for comment on the cell dimensions of thorite.

<sup>†</sup> Slightly differing cell dimensions for monazite have been published by v. Gliszczynski (1939), Machatschki (1941), Kokkoros (1942) and others.

Dubinina (1939). In the first of these papers it is stated that "This pattern has only lines with rather weak intensity as consequence of transformation of nearly whole mass of mineral to metamict state, i.e., isotropic state of secondary origin." It will be seen from Table 3 that the cell volume of thorite given there is quite out of line with that of other members of the zircon and monazite groups. Also some of the indices assigned to powder lines by Boldyrev et al. are not in conformity with the space group I4/amd and the writer has found that the published pattern does not fit well an ideal set of spacings calculated from the given cell dimensions. Hence those dimensions are to be regarded with some reserve.

It is of interest to consider a possible explanation of the fact that the tetragonal form of thorium silicate is characteristically found in the metamict condition whereas the newly recognized monoclinic form occurs entirely in clear crystal fragments showing not the slightest trace of alteration. This may be correlated with observations on the better known relatives of these two minerals. Zircon has frequently been found in the metamict state whereas monazite is rarely, if ever, found in this condition. It has been suggested by Machatschki (1941) that the metamict condition of zircon arises due to an inherent instability of the structure of zircon. In this zirconium has an 8-fold coordination, whereas the radius of Zr<sup>+4</sup> is near the boundary of 6 and 8-fold coordination and in many minerals Zr<sup>+4</sup> goes into 6-coordinated positions. It may then be that the huttonite structure is more stable than the thorite structure though it is not possible at this time to state precisely what the differences in the two structures are.